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KRAFT PULPING EFFLUENT TREATMENT AND REUSE: STATE OF THE ART

W. G. Timpe, et al

Saint Regis Paper Company
Pensacola, Florida

February 1973

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KRAFT PULPING EFFLUENT TREATMENT AND REUSE - STATE OF THE ART

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The results of the survey include information on activated carbon and its applications in treatment of pulp and paper mill effluents as well as in treatment of municipal water supplies and effluents. Information is presented on lime treatment of kraft mill effluent and on other advanced treatment methods. It also covers the subjects of in-plant water reuse, effluent collection systems, solids removal, and biological oxidation.

This report was submitted in partial fulfillment of Grant #12040 EJU between the Environmental Protection Agency and St. Regis Paper Company.

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SECTION I

CONCLUSIONS

The following conclusions have been reached:

Activated Carbon

1. Activated carbon is being used commercially and/or tested in large scale pilot plants for municipal water and effluent treatment, as well as in diverse industrial applications.

2. Specific information and the extent of current development activity by others encourages proceeding with the program to develop the use of activated carbon for water renovation in kraft pulp and paper mills.

3. Activated carbon for pulp and paper mill effluent application has been and is being studied on a laboratory and small pilot plant basis by several investigators. Its application is usually considered as a polishing step. Most of the work has been with granular activated carbon which necessitates regeneration. Most work is on caustic bleach plant effluent; some on total effluents and on evaporator condensate. No work on turpentine separator underflow has been reported in the literature.

4. Carbon selection must be based, it was confirmed, on specific test work with actual waste water. Standard carbon characterization tests are useful only as guidelines, together with recommendations based on experience, to narrow the number of carbons to be specifically tested and compared for a given application. A strong contributing factor in this situation appears to be the incomplete characterization of most solutions that are to be treated.

Water Usage and Recycle

1. The pulp and paper industry uses 2,100 billion gallons of water annually.

2. Reuse of water is extensively practiced in the industry. Reuse practices consist mostly of in-plant reuse rather than total mill effluent reuse.

3. In-plant reuse may involve treatments such as solids removal or cooling, but generally does not involve removal of dissolved organics.

4. In-plant reuse includes both in-process reuse (such as recycle

of paper machine white water) and downgrading, process to process reuse (such as use of bleach plant effluent in the woodyard).

5. Effluent flows range from 10,000 to about 60,000 gallons per ton of unbleached kraft.

6. Effluent flows of 4,000 to 6,000 gallons per ton might be achieved through improved design and increased in-plant reuse, still without resorting to removal of dissolved organics.

7. One current study is aimed at total mill effluent treatment and recycle using alum precipitation and biological oxidation.

Present Effluent Treatment Methods

1. Present treatment systems provide for the removal of suspended solids and biologically oxidizable materials. Such treatment does not remove color bodies from the effluent.

2. Effluent quality obtained by these conventional methods, even if these methods were employed more fully within their limits, is not acceptable for most kraft mill feed water requirements.

Advanced Treatment Methods (other than activated carbon)

1. Lime treatment (precipitation) is the most actively pursued advanced treatment method. It is aimed at color removal before biological oxidation and effluent discharge.

2. Other precipitation-coagulation methods have been investigated, but only alum treatment is still being pursued with some promise (see conclusion B,7).

3. Reverse osmosis is under active investigation in the sulfite pulping industry for the concentration of wastes and production of reusable water.

4. These advanced treatment methods, particularly the lime treatment, deserve further consideration as part of a treatment system involving activated carbon to produce reusable treated effluent.

SECTION II

RECOMMENDATIONS

Continuation of this program is recommended with the next major step being a laboratory program to be outlined in detail. The conclusions of the survey indicate that two approaches should be pursued to lead to maximum water reuse, i.e. treatment of total mill effluent and separate treatment of in-plant effluents to extend the existing trend of in-plant recycle and reuse. The treatment of total mill effluent and bleach plant effluents by carbon and various combinations of carbon and biological oxidation and lime treatment should be investigated, while for the other in-plant effluents, carbon treatment alone should be investigated for removal of dissolved organics.

It is recommended that a broad range of commercial carbons be investigated since the adsorptive and physical characteristics of the activated carbon to be produced by the St. Regis recovery process are as yet unknown. It is recommended that this investigation then be used to define the desired characteristics which the St. Regis carbon should have.

It is recommended that effluents from several St. Regis southern kraft mills be used in the laboratory investigation since effluents are insufficiently characterized to date and are known to vary in time and place.

SECTION III

INTRODUCTION

Program Overview

Under a Federal Water Quality Administration (FWQA) contract, St. Regis Paper Company has been engaged since July, 1969, in a program for the development of an economical system for maximum water reuse in the kraft pulp and paper industry as a means of water pollution control and water conservation. This program is based on two key concepts: (1) effluent treatment using activated carbon and, (2) on-site production of activated carbon from readily available raw materials, particularly black liquor, with full integration into the kraft mill recovery and power systems to achieve the lowest net cost of activated carbon.

An earlier order-of-magnitude economic estimate for an unbleached kraft pulp and paper mill indicated that effluent treatment and reuse, based on activated carbon, produced at the mill, promises to be competitive with treatment and discharge, based on the lime treatment pioneered by the National Council for Air and Stream Improvement (NCASI) (63). A premise of this comparison is that effluents of less than lime-treated quality will become unacceptable in the foreseeable future.

St. Regis Paper Company made application to the Federal Water Quality Administration for a Research and Development Grant for this work as provided in the "Clean Water Restoration Act of 1966".

St. Regis Paper Company on June 23, 1969, accepted an FWQA Research and Development Grant (12040-EJU) of $878,472, representing an average of 59% of eligible estimated project costs of $1,483,862. Under the program, the two key concepts (i.e. of effluent treatment with activated carbon, and of activated carbon production), are being pursued in two separate but interdependent programs. Part I is the program concerned with the development of effluent treatment with activated carbon. A portion of this program is the subject of this report. Part II is the program concerned with the production of activated carbon. This will not be discussed further in this report.

Part I of this program was initiated in July, 1969, with a literature and very limited industry survey. This survey was completed during October, 1969 and forms the basis of this report.

Objective and Scope of Survey

This survey was primarily mission oriented. It was intended to provide, and has provided, for the project team information necessary or useful in formulating development strategy and determining laboratory procedures.

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It is unavoidable in such an effort that information not strictly pertinent or necessary for the task at hand is included. The short time allowed for completing the survey, on the other hand, makes it likely that some pertinent literature has been overlooked, and that a number of active developments have not been assessed. The "survey" is therefore of necessity a continuing effort with the objective of incorporating most up-to-date information in this development. However, only the initial survey is covered in this report.

The technical coverage included activated carbon, its properties, methods of application, and utilization, particularly in effluent treatment. It also included present and proposed paper industry in-plant water reuse schemes; effluent treatment systems including collection systems, solids removal, biological treatment, and coagulation and precipitation treatment methods, particularly those involving lime. To a very limited extent information was included on processes of potential future interest but not covered in the preceeding categories, particularly hyperfiltration (reverse osmosis) and ion exchange.

The literature survey included a search of Chemical Abstracts V. 45, 1951 through V. 70, 1969; and Water Pollution Abstracts V. 40, 1967, through V. 42, No. 3, March 1969. The following terms were searched: Wastes, Water pollution, Water purification, Sulfite liquor, Sewage, Paper, Pulp and paperboard waste liquors, Ion exchange for waste water, Water-potable and industrial. This search did not include small water purification systems or specific locations. Emphasis was placed on those items pertaining to the pulp and paper industry.

The literature survey also included perusal of the Bulletins published by the National Council of the Paper Industry for Air and Water Improvement (NCASI), FWQA reports, and a review of direct access to pertinent recent technical publications and journals.

A very important part of the survey consisted of personal discussions with representatives of manufacturers of activated carbon, with technical personnel involved in the various pilot and commercial applications of activated carbon in water and effluent treatment, and with operating and engineering personnel in the paper industry.

SECTION IV

ACTIVATED CARBON

General Information

1. Manufacture

Activated carbon can be prepared from any carbonaceous material, but only a limited number of materials are used commercially. Activation of carbon is accomplished by two general methods (93):

(1) High-temperature controlled oxidation of a previously charred carbonaceous material.
(2) Lower temperature chemical activation of carbonaceous raw material.

Most of the production in the United States utilizes the high-temperature process, however, the chemical activation is favored in Europe.

2. Types and Physical Properties

Activated carbon is manufactured either in a powdered or granular form. The powdered form has generally been used for purifying liquids whereas the granular form has been used for gas purification. In recent years, there has been an increasing usage of granular carbon for liquid purification.

Activated carbon is characterized by an extremely large surface area (450-1800 sq.m/g) per unit weight. Pore volume and pore volume distribution are characteristics that affect the use of a carbon as an adsorbent.

3. Manufacturer's Information

Manufactures generally list several specifications for their carbons. Common specifications are mesh size, iodine number, molasses number, methylene blue number (these numbers are a measure of the adsorptive capacity for these three compounds under standardized test conditions), abrasion number, ash content, pH of water extract, and various density measurements. The specifications given by a manufacturer can only be used as a very rough guide to carbon selection for a particular application. The results of one study show that competent and justifiable selection can only be achieved by evaluating the carbon on the particular effluent under consideration (10).

TABLE I lists information on several commercially available activated carbons.

4. Laboratory Evaluation

Laboratory evaluations of the adsorptive capacity of activated carbon are generally based on the empirical Freundlich equation which relates the amount of impurity in the solution phase to the impurity in the adsorbed phase. The Freundlich equation is as follows:

TABLE I

Properties of Selected Activated Carbons

Carbon	Principal Application	Base Material	Standard Form[e]	Pore Volume[f], cc/g	Mean Pore Size[f], A°	Nitrogen Area[f], m^2/g	Iodine Number[f]	Moisture[g] %	Price in Car Load[g] Lot, $/lb
Aqua Nuchar (a)	Water Treatment	Black Liquor	Powd.	0.4 to 0.6	20	754	703	5	0.085
Nuchar C-190 (a)	Chemical Purification, Sugar Decolorization	Black Liquor	Powd.	0.9	30	700-900	1071	3	0.14
Darco S-51 (b)	Chemical Purification, Sugar Decolorization	Lignite	Powd.	1.0	30	700	1159	12	0.135
Darco KB (b)	Vegetable Oil Decolorization and Purification	Wood	Powd.	2.2	26	1200	1200	33	0.29
Barneby Cheney SC	Water Treatment, Decolorization	Nut Shell	Gran.	-	-	-	-	5	0.32
Norit Poly-C (c)	Water Treatment	Wood	Powd.	1.1	-	400	-	10	0.24
Norit A (c)	Vegetable Oil Chemical, Water Purification	Wood or Peat	Powd.	0.5	35	750	-	10	0.17
Norit F (c)	Vegetable Oil Chemical, Water Purification	Wood or Peat	Powd.	0.4	-	640	-	10	0.115
Norit SG (c)	Vegetable Oil Chemical, Water Purification	Wood or Peat	Powd.	-	-	750	-	12	0.26
Filtrasorb 100 (d)	Water Treatment	Coal	Gran.	-	-	800-900	800	2	-
Filtrasorb 300 (d)	Municipal Effluent	Coal	Gran.	0.8	25	950-1050	900	2	-
Filtrasorb 400 (d)	Municipal Effluent	Coal	Gran.	0.9	35	1000-1100	1000	2	0.29

a) Chemical Div., Westvaco b) Atlas Chemical Ind. c) American Norit Co. d) Calgon Corp. e) Powdered carbons are 90% minus 325 mesh except S-51 (70%) and KB (50%) f) Dry basis g) "As is" basis.

$$x/m = kc^{1/n}$$

where:

x = amount of impurity adsorbed

m = weight of carbon

x/m = concentration of impurity in adsorbed state

c = concentration of impurity in solution at equilibrium with impurity in adsorbed state

k,n = constants

A plot of x/m versus c on log-log graph paper yields a straight line from which the theoretical ultimate capacity of the carbon may be obtained by extrapolation. A complete description of techniquies used to establish adsorption isotherms is presented by a number of authors (91, 44, 16).

Adsorptive Properties

1. Surface Area

Adsorption is usually explained in terms of the surface tension (or energy per unit area) of the solid (15). Molecules in the interior of any solid are subjected to balanced forces, whereas surface molecules are subjected to unbalanced forces toward the interior. The inward forces can only be satisfied if other molecules, usually liquid or gaseous, become attached on the surface of the solid. The forces of attraction, or Van der Waal's forces, are relatively weak, and adsorption due to these forces is called physical adsorption because the adsorbed species is easily removed from the adsorbent. A stronger, irreversible type of adsorption can occur as the result of chemical interaction between the adsorbate and the adsorbent. Adsorption due to chemical interaction is called chemisorption. Both physical and chemisorption are included in the general term sorption.

Although there is presently no method of measuring the surface tension of a solid directly, it is known that the total surface energy is equal to the product of the surface tension and the total area. For this reason, high surface area is a prerequisite for good adsorption. As mentioned previously, activated carbons have surface areas ranging from 450 to 1800 sq.m/g.

It is known that activated carbon is effective for removal of organic substances of relatively low water solubility, primarily because of the large interfacial area on which such substances may accumulate (97). It is apparent, however, that an explanation of the adsorptive capacity of activated carbon based entirely on surface area is far from complete. Equal

weights of two active carbons which have equal surface area, but have been prepared from different raw materials and/or by different processes may function quite differently as adsorbents.

Two phenomena have been presented to account for this difference in adsorptive ability of carbons having equal surface area. Part of the explanation is based on relative pore size distribution while another part of the explanation is based on the surface chemistry of the carbon.

2. Pore Size Distribution

As shown in Figure 1, gas-phase carbons and liquid phase or decolorizing carbons exhibit different pore size distributions. Gas-phase carbons show pore-volume peaks in the microporous range (3 to 50 Å radius) and in the macroporous (1000 to 50,000 Å radius) range, whereas decolorizing carbons exhibit peaks in these ranges as well as in a transitional (50 to 1000 Å radius) pore range (93). A large amount of transitional pore volume gives an open structure favorable to access by solutions or liquids, resulting in rapid attainment of adsorption equilibrium for smaller adsorbates. The accessibility to larger molecules and colloidal substances is also improved by pores in this range. The significant difference in pore volumes associated with activated carbon made from different raw materials by different processes is the magnitude of the pore volume concentration in the various pore size ranges.

3. Surface Functionality

The nature of the carbon surface is another property that affects the adsorption capacity. Activated carbon is not an inert material; it exhibits acid-base properties and it can undergo several chemical reactions such as halogenation, oxidation, and hydrogenation (93). Several authors have discussed the surface nature of activated carbon and the effect of certain functional groups on the sorptive power exhibited by a carbon (97, 27).

Snoeyink and Weber (97) presented a discussion on the surface chemistry of activated carbon and how the various functional groups associated with carbon surfaces can affect adsorption capabilities. The nature of these functional groups is determined to a large extent by the method of activation as well as by the starting raw material. Two major types of surfaces were postulated for activated carbons: (1) uniform planar surfaces and (2) heterogeneous edges of planes characterized by various types of functional groups and vacancies due to the action of oxidizing gases. Most of the surface area of a carbon particle is in the micropores and is of the uniform planar type. Most of the adsorption occurring on this type sur-

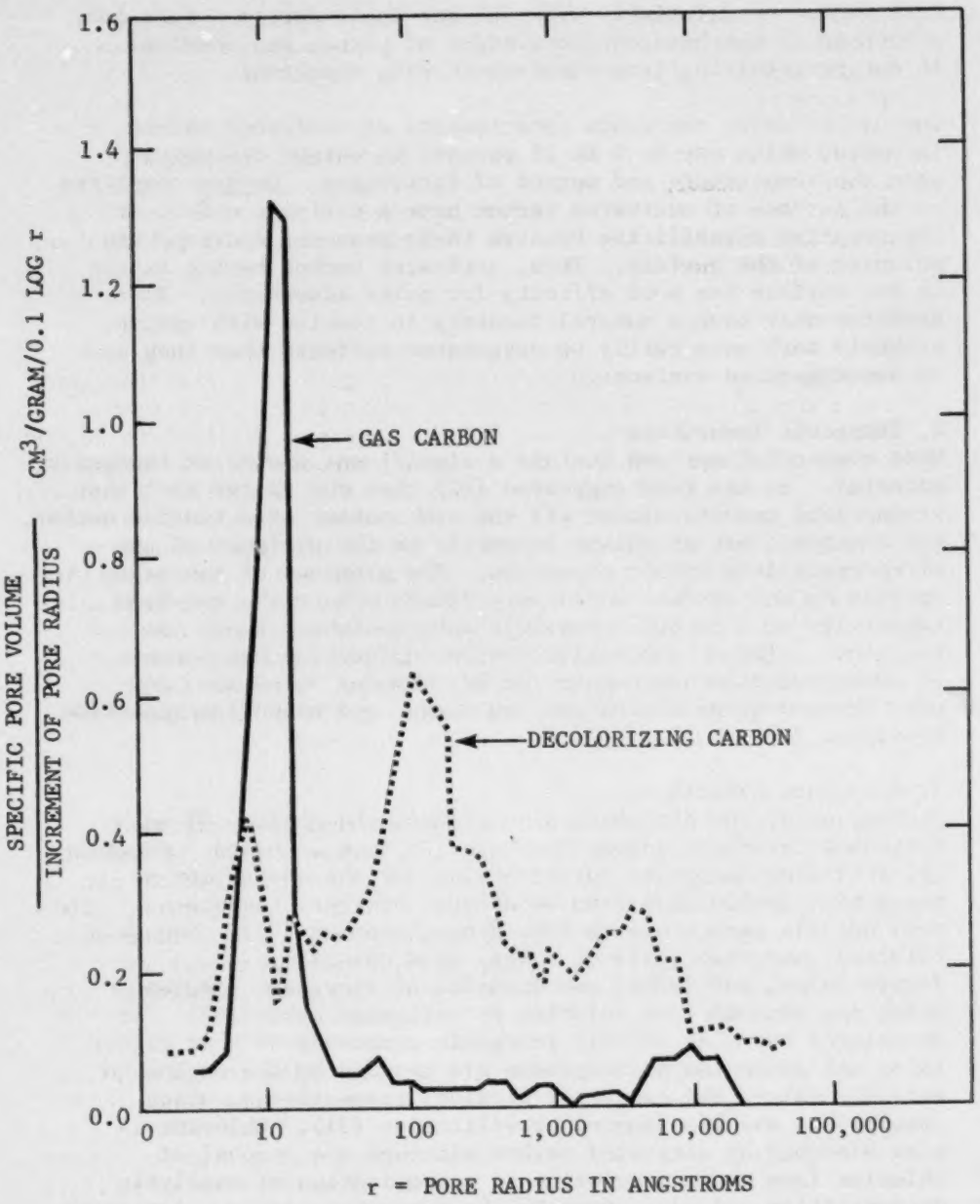

Figure 1

Pore Volume Distribution of Typical Activated Carbons (93)

face is due to relatively weak Van der Waals forces. Sorption processes at the heterogeneous edges of planes are chemical in nature resulting from electron-sharing reactions.

One of the major noncarbon constituents of activated carbon is oxygen which may be 2 to 25 percent by weight depending upon the temperature and method of activation. Oxygen complexes on the surface of activated carbon have a definite effect on the sorptive capabilities because their presence increases the polarity of the surface. Thus, activated carbon having oxygen on the surface has more affinity for polar adsorbates. Also, sorbates that have a natural tendency to combine with oxygen probably sorb more easily on oxygenated surfaces than they do on nonoxygenated surfaces.

4. Inorganic Impurities

Most commercial carbons contain a significant amount of inorganic material. It has been suggested (97) that due to the fact that strong acid removes almost all the ash content of activated carbon, the inorganic matter exists primarily on the surfaces of the microcrystallite carbon structure. The presence of inorganic species on the surface would very likely affect the sorption capability of a carbon. Possible interactions between the inorganic salts on the active carbon surface and the sorbate or other solution components include complex formation, ion-pair formation, precipitation reactions, and oxidation-reduction reactions (97).

5. Adsorbate Effects

The nature of the adsorbate also affects the ability of an activated carbon to adsorb that species from solution. Generally, activated carbon is not effective for the adsorption of inorganic electrolytes from solutions, however, there are some notable exceptions to this generalization (91). Mercuric chloride, molybdate, silver salts, gold chloride, ferric salts, and iodine are examples of inorganic species which are removed from solution by activated carbon(88). It is pointed out that certain inorganic compounds such as silver salts and potassium permanganate are reduced by the carbon to metallic silver and manganese dioxide, respectively, which precipitate and are removed by filtration (91). Chlorine is also adsorbed by activated carbon although the removal of chlorine from aqueous solution is a combination of catalytic decomposition and adsorption by the activated carbon. Activated carbon treatment usually precedes chlorination in water treatment plants because of its ability to remove chlorine from water and because it will remove some of the chlorine-consuming organics.

As a general class, organic compounds are adsorbable. The

higher molecular weight organic compounds are generally more amenable to adsorption than are low molecular weight compounds. Colloidal organic compounds are not readily adsorbed because these compounds cannot penetrate the pores of the activated carbon particle (10). Strongly hydrophilic (polar) organic compounds such as carbohydrates or other highly-oxygenated organic material are generally refractory to carbon treatment. Sugars and low-molecular weight glycols, amino acids, hydroxy acids, sulfates, and sulfonates are all very water soluble and poorly adsorbable on carbon (10). Molecular configuration also influences the ability of carbon to adsorb organic molecules and in some cases steric hindrance would prevent the molecule from entering a pore.

6. Temperature Effect on Equilibrium and Rate

The effect of temperature on adsorption, especially from liquid solutions, is not easily predicted. Since adosrption is a thermodynamically exothermic process, increasing the temperature should decrease adsorption capacity (46). Although gas-solid systems usually adhere to the predicted behavior, many solid-liquid systems appear to contradict the predicted effect of temperature. Substances, such as an aqueous solution of n-butyl alcohol, that have a negative solubility coefficient will not be as soluble at higher temperatures and adsorption will thus be increased. Fuchs (46) found that increased temperature increased the adsorption of color from pulp mill bleach plant caustic extract on activated carbon. He explained this phenomenon by decreased liquid surface tension at higher temperatures. The decreased surface tension at higher temperature results in increased "wetting" or penetration of the liquid into the pores of the carbon.

The rate of adsorption is also affected by temperature changes. Investigations by Morris and Weber (77) and by Weber (104) on the kinetics of adsorption on granular carbon in rapidly stirred batch systems indicate that the rate of adsorption is controlled by the rate of diffusion of solutes in the internal capillary pores of the carbon particles. Assuming that the rate of adsorption is in fact controlled by the rate of diffusion of solute particles into carbon capillaries, the effect of temperature can be shown by the following equation (46):

$$D_{AB} \propto K^{T}/\mu_B$$

Where: D_{AB} = Diffusivity of solute A thru solvent B

K = Constant, dependent upon solvent and solute

T = Absolute temperature

μ_B = Viscosity of solvent

Thus it is seen that rate of diffusion and, in turn, the rate of adsorption increases with increasing temperature. The advantage of increased adsorption rates with increasing temperature can be utilized in laboratory evaluation of adsorption isotherms. Smith (96) has suggested maintaining solution temperatures (Kraft effluents) near the boiling point for laboratory isotherm determinations. Using finely ground carbon samples and high temperatures, equilibrium will be established in two to three minutes, but there will be little effect on the equilibrium itself.

7. Effect of Particle Size

Since the controlling factor on the rate of adsorption usually is the rate of internal diffusion, it would be expected that adsorption rates would increase with decreasing particle size. Morris and Weber (77) have experimentally shown that the rate of adsorption is inversely proportional to the diameter squared. In laboratory evaluation of granular activated carbon it is recommended to pulverize the carbon so that 95 to 100% passes through a 325 mesh screen (16,61). This will eliminate the variable of particle diameter on adsorption rate studies, although the equilibrium capacity will be affected slightly. Pulverizing the carbon will increase the equilibrium capacity to a small extent because of increased external area and because previously "blind" pores will become available as adsorption sites. The effect is quite small because the majority of the adsorptive capacity is due to internal surface area.

8. Effect of p^H

The p^H of the solution being treated may profoundly affect the adsorption of solutes. One report (78) says that adsorption is best when the water is slightly acid or neutral, although carbon is effective up to p^H 9.0. Helbig (60) emphasizes that the statement "that carbons adsorb more effectively in acid solutions than in alkaline solutions" should not be used as a criterion without qualification. The principal effect of p^H on carbon adsorption is probably indirect, due to its influence on solubility of the adsorbate. Generally, maximum adsorbability occurs at minimum solubility, a phenomenon which frequently occurs in the alkaline p^H range as it does, for example, with alkaloids. Increased adsorption of color from pulp and paper mill caustic extract occurs at decreased p^H levels (46). This is probably accounted for by the decreased solubility of lignin at lower p^H values as evidenced by its precipitation at a p^H of two.

Adsorption Processes

In the next few paragraphs a brief description of the basic mechanics of utilizing granular and powdered activated carbon will be given.

1. Granular Carbon

Granular carbon is usually used in a vertical cylindrical column (43). There are two basic types of column systems, namely, the fixed bed and the moving bed systems. Fixed bed columns may be used singly or as multiple column systems arranged either in parallel or in series. Moving bed systems may be of the continuous or the pulsed bed type.

The simplest arrangement is the single fixed bed column. Fornwalt and Hutchins (45) indicate that a single-column system is preferentially used in the following situations:

(1) The breakthrough curve of the carbon is steep.
(2) The carbon charge will last so long at the desired processing rate that the cost of replacing or regenerating it becomes a minor part of operating expense.
(3) The capital cost of a second or third column cannot be justified because carbon savings will not pay for additional equipment.
(4) For some reason (such as prevention of crystallization or product deterioration) an unusual temperature, pressure, or other controlling condition must be maintained in the column.

Multiple-column systems are used in cases where the process cannot be interrupted for unloading, reloading, or regeneration, and a standby column is not available; or if the available space limits the size or height of the column (45).

Figure 2 is a simple schematic of multiple columns arranged in series. Series-column systems are used if: (1) the break through curve is gradual and a highly purified effluent is desired or (2) it is economically necessary to completely exhaust each pound of carbon because of a gradual breakthrough curve and a high carbon requirement per unit of production (45). These units are operated downflow and each carbon bed is replaced as a complete batch. As shown in the schematic the effluent from one column becomes the influent of the next column. An extra column is required. When breakthrough occurs (some controlling parameter such as BOD, color, COD, etc. exceeds the desired value in the purified liquid) the lead column is taken out of the system and the unused bed becomes the last column. The carbon in the first column is regenerated and the next time breakthrough occurs the second column is taken out of service and the first column containing regenerated carbon is placed in the series as the last column. In this manner the carbon beds are used countercurrent to the waste flow so that the liquid having the lowest level of contaminants is contacted with the freshest carbon.

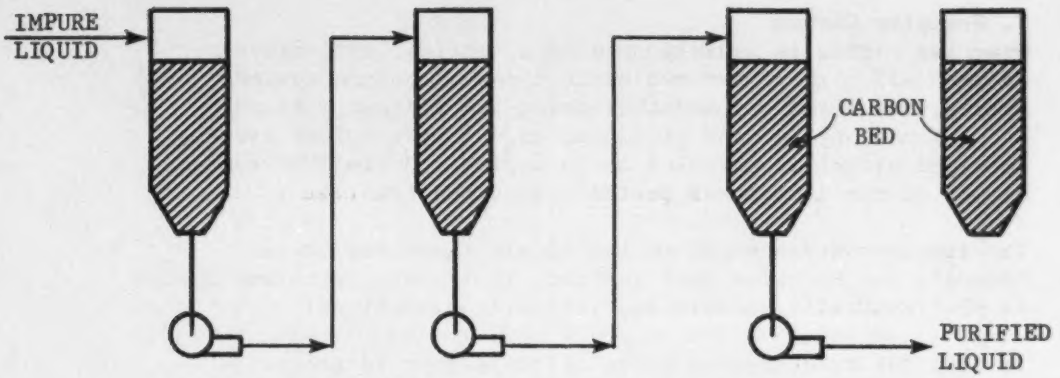

Figure 2

Multiple Column System with Columns Arranged in Series

Another multiple column system is the arrangement of the columns in parallel and the utilization of either upflow or downflow through the columns. When a high degree of organic removal is not necessary, this arrangement can be used (70). The columns are placed into operation at evenly spaced intervals, thus when one column is nearing exhaustion another is being started up on freshly-regenerated carbon and the other columns are at various intermediate stages of exhaustion. Since the columns discharge into a common manifold, the blended material from the columns will meet specifications if they are designed properly. This system requires smaller pumps, less power, and less stringent pressure requirements for columns and piping than columns operated in series (45).

Methods of designing granular carbon columns for treating municipal wastewater were described by Allen (1). Moving bed systems have a number of advantages over fixed bed series systems. In the moving bed system the liquid flow is upward, and fresh carbon is added to the top of the column as spent carbon is withdrawn from the bottom (45). Thus, the flow of carbon is countercurrent to the flow of water which provides a high loading of impurities on the carbon. Also, plugging of the bed is avoided by the upflow of water (57). The utilization of moving beds is of principal importance in larger units where the lower capital investment, compared with columns in series, is of importance. With the possible exception of instrumentation costs, this system comes the closest to completely exhausting the carbon with the minimum capital investment (45).

2. Powdered Carbon
Powdered activated carbon is used to treat liquids by the layer filtration method, batch contact system, multistage countercurrent flow system, or the divided flow system (43).

Layer filtration involves making a slurry of powdered carbon in a suitable liquid. A precoat carbon filter cake is then formed on the filter cloth of a filter and the liquid to be treated is allowed to flow through the precoat.

In the batch contact system, carbon is added to a tank of liquid, the contents are agitated, and the carbon is removed by filtration.

To reduce the amount of powdered carbon needed, multistage countercurrent and divided flow systems are used. In the multistage countercurrent system the carbon is used more than once. For example, in a two stage countercurrent system two sets of carbon contact tanks and two sets of filters are used. In the first tank, untreated liquid is mixed with carbon that has already been used in the second tank. In the second tank, the partially-purified liquid is contacted with fresh carbon. This process is best for a product that is made continuously.

For liquids that have to be treated only intermittently, countercurrent treatment is not feasible because it is impractical to store partially-spent carbon. In this system, as shown in Figure 3, the solution is purified in two stages, using fresh carbon at each stage.

Adsorption Applications

1. Water Treatment
Hager (55) has described the use of granular activated carbon for water treatment at Nitro, West Virginia. The water treatment plant treats water from a river heavily polluted with various organic and industrial wastes and before the use of activated carbon the odor and carbon-chloroform extracts (CCE) of the treated water frequently exceeded recommended levels. Using 14x40 mesh granular carbon beds as combination filter-adsorption units, an average of 8 mgd of water are treated. Treatment ahead of the carbon beds consists of double aeration to remove volatile components, after which the water enters a 24-hour sedimentation basin where alum is added as a coagulant and chlorine is added as a disinfectant. After coagulated impurities have settled out, the water is passed through the carbon beds. Table II depicts the reported capability of the carbon. On-site regeneration of the spent carbon is accomplished in a multihearth furnace.

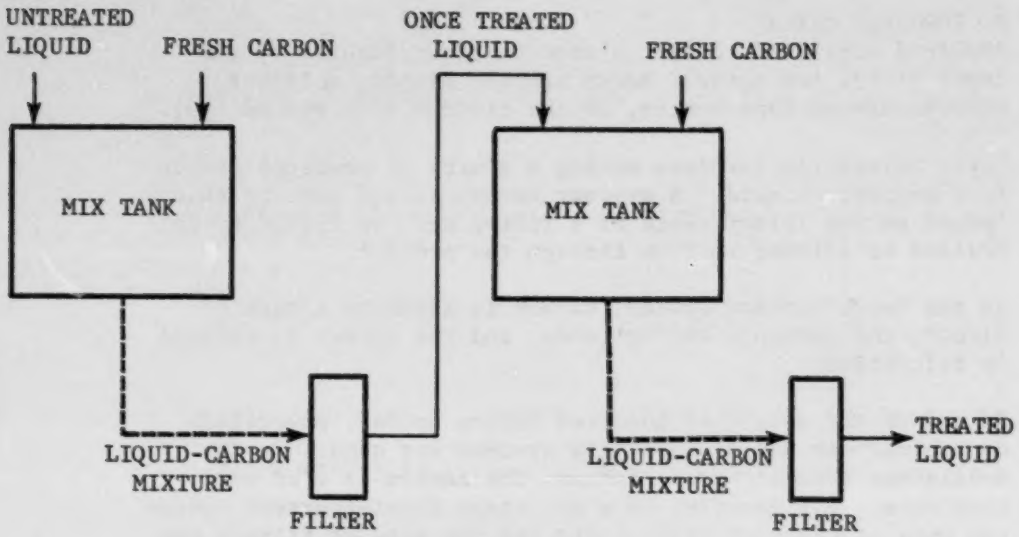

Figure 3

Divided Feed Application of Powdered Carbon

Table II

Activated Carbon Treatment of Water at Nitro, W. Va.

Test Parameter	Raw Water	Applied to Filters	Recommended Standards	Finished Water
Threshold Odor No.	66-333	30-50	3	0-3
Turbidity (Jackson units)	-	5-15	5	0.05
Carbon-Chloroform Extract Value (ppb)	-	200	200	50

In the last few years that has been intense interest in the use of activated carbon to treat municipal and industrial wastewater. Although there are some plant-scale installations, most of the investigations have been pilot-scale or laboratory evaluations.

2. Municipal Effluents

One commercial installation for the treatment of municipal waste by activated carbon is operated by the South Tahoe Public Utility District in California (29,28). Effluent from a conventional activated sludge process is coagulated with alum and filtered through mixed-media filters in series. Effluent from the filters is then passed through two upflow, countercurrent granular activated columns in parallel. Table III depicts the effectiveness of the plant in removing impurities. The final effluent was colorless, odorless, and had a turbidity of less than 0.5 Jackson Units. The granular carbon beds reduced the

Table III

South Tahoe Public Utility District - Overall Plant Efficiency (29)

Test Parameter	Raw Waste	Activated Sludge Effluent	Effluent from Filters	Chlorinated Carbon Column Effluent
B.O.D., mg/l	200-400	20-40	1	1
C.O.D., mg/l	400-600	80-160	30-60	3-16
Total Organic Carbon, mg/l	-	-	10-18	1-6
Suspended Solids mg/l	160-350	5-20	0.2-3.0	0.5
Turbidity, units	50-150	30-70	0.2-3.0	0.5
Phosphates, mg/l	15-35	25-30	0.1-1.0	0.1-1.0
A.B.S., mg/l	2-4	1.1-2.9	1.1-2.9	0.002-0.5
Coliform Bacteria, MPN/100 ml	$15x10^6$	$15x10^4$	15	2.2
Color, units	High	High	10-30	5
Odor	Odor	Odor	Odor	Odorless

C.O.D. from the 30 to 60 mg/l range to the 3 to 16 mg/l range. The influent to the carbon column had a total organic carbon (TOC) content of 10 to 18 mg/l while the effluent from the carbon treatment contained 1 to 6 mg/l TOC. The treatment facilities also privide for carbon regeneration in a multiple hearth furnace.

An 0.3 mgd granular activated carbon pilot plant at Pomona, California has been in operation since 1965 under the direction of the Federal Water Pollution Control Administration and the Los Angeles County Sanitation District. The plant uses a four-stage, packed-bed, downflow, granular activated carbon column to treat effluent (primarily domestic) from a contact stabilization activated sludge treatment (35). The spent carbon is reactivated in a multihearth furnace. Table IV lists the average water quality characteristics obtained in more than a year of operation.

Table IV

Average Water Quality Characteristics - Pomona Pilot Plant (35)
(June, 1965 - August, 1966)

Parameter	Column Influent	Column Effluent
Suspended Solids, mg/l	10	1
C.O.D., mg/l	47	9.5
Dissolved C.O.D.,mg/l	31	7
T.O.C., mg/l	13	2.5
Nitrate, as N, mg/l	6.7	3.7
Turbidity, JTU	10.3	1.6
Color	30	3
Threshold Odor	12	1

It was observed that dissolved oxygen decreased and carbon dioxide increased as the effluent passes through the carbon columns. These observations, plus the fact that the average nitrate-nitrogen decreased, led investigators to believe that the column performance was being enhanced by biological activity. Further tests, using small carbon columns showed that activated carbon columns can be used to reduce the nitrate in highly nitrified effluents to less than 10 mg/l. It was found that supplemental organics would have to be fed to the column to

achieve more than the 3 mg/l that is removed routinely. Methanol in amounts equivalent to 20 and 40 mg/l of COD was fed to a small column receiving 25 mg/l of nitrate (as nitrogen) for extended periods. This increased the nitrate removal up to 15 mg/l (as nitrogen).

Joyce, et al., performed laboratory and pilot scale evaluations of the use of granular activated carbon to treat secondary effluent from the activated sludge treatment system at the Pleasant Hills Treatment Plant in suburban Pittsburgh (2). They judged the effectiveness of the system by the degree of COD and ABS removal. The secondary effluent was pretreated by passage through a sand filter, and downflow columns in series were used for the carbon treatment. The COD content was reduced from the 50 to 70 mg/l range to the 12 to 20 mg/l range under a variety of operating conditions. Refractory organics such as ABS were eliminated completely.

Beebe and Stevens (4) investigated the use of powdered activated carbon in a pilot plant operated at 7 to 9 gallons per minute. The trials, conducted on activated sludge effluent from the Tucson Municipal Sewage Treatment Plant, used an Accelator (trademark of Infilco) recirculating slurry contact treatment unit having a nominal treatment capacity of five gallons per minute. To prevent excessive carryover of carbon it was found necessary to coagulate the carbon particles. A dosage of 15 mg/l of ferric sulfate and 0.5 mg/l of cationic polyelectrolyte were applied to the primary mixing zone and to the coagulating zone respectively. The effluent from the Accelator was filtered through sand filters. The following table shows the capability of the process during a run using a carbon dosage of 138 mg/l. Effluent from the sand filter was chlorinated and analyzed with respect to the Public Health Service's 25 physical and chemical drinking water standards. The product water quality met or exceeded 23 of 25 drinking water standards.

Table V

Results of Run No. 3 - Tucson Pilot Plant (4)

Test Parameter	Influent to Carbon Unit	Effluent from Sand Filter
Turbidity, units	17.6	1
Color, units	15.7	3.6
C.O.D., mg/l	36	14
A.B.S., mg/l	4.2	0.25

A ten gallon per minute pilot plant using powdered activated carbon is being operated by FWPCA personnel at the Lebanon, Ohio Municipal Sewage Treatment Plant (70). The powdered carbon adsorption pilot plant uses two stage countercurrent adsorption with three tanks per stage (102). The first tank is an agitated contact tank providing two to seven minutes retention time for the influent from an activated sludge treatment system. Polyelectrolyte is added at a dosage of 1 to 3 mg/l to the effluent in the pipeline between the first and second tanks. The second tank is a flocculation tank providing 15 minutes retention time. The third tank is a sedimentation tank.

Carbon dosages ranged from 100 to 300 mg/l and a secondary effluent concentration of 15 ppm total organic carbon was reduced to 1.5 ppm. If a primary effluent was used, secondary-treated quality water was obtained. Table VI presents a summary of results from several trials of treating primary effluent with powdered activated carbon (70).

Table VI

Treatment of Primary Effluent by Powdered Carbon, Lebanon, Ohio (70).

Run	Carbon, mg/l	Flow, gpm	Polymer, mg/l 1st Stage	Polymer, mg/l 2nd Stage	Primary Effluent T.O.C., mg/l	Primary Effluent Turbid. JTU	Powdered Carbon Effluent T.O.C., mg/l	Powdered Carbon Effluent Turbid. JTU	Filter Run Hr.
3	200	5	1.0	1.5	69.0	41.7	10.2	3.3	27
5	200	5	1.0	1.5	41.7	23.4	3.7	1.0	22
6	200	5	1.5	1.5	46.3	28.5	4.1	2.2	29
7	200	5	1.5	1.5	48.4	30.5	6.7	2.9	22
9	300	5	1.5	3.0	67.1	45.0	11.0	1.2	24

In a study of treating municipal waste water with powdered activated carbon (42), it was found that surface area in pores greater than 14Å in radius gave the best correlation with TOC adsorption capacity of several commercial carbons. It was concluded that for absorbing organics from municipal waste water, the carbon should have a broad spectrum of pore sizes.

A plant designed to treat 10 mgd of municipal waste water at Rocky River, Ohio, by granular activated carbon following primary

clarification has been described (17). This design uses eight down-flow single-stage columns operated in parallel, each 16 ft. in diameter and 25 ft. high to reduce BOD by 85%.

3. Pulp and Paper Applications

Several investigators have evaluated the capabilities of activated carbon in treating various pulp and paper mill effluents. These investigations have been on a laboratory and small pilot-scale basis. No commercial applications have been reported.

Hunt (65) investigated nine different activated carbons for decolorizing a 50/50 mixture of acid and caustic semi-chemical bleaching wastes. Adsorptive capacities (in terms of volume of liquid treated per unit weight of carbon) at 100% decolorization ranged from 180 to 288 ml/g.

Investigations of color removal from a 50/50 mixture of acid and caustic semi-chemical bleaching wastes by powdered and granular activated carbon, activated alumina, and mixtures of these absorbents has also been reported (110). Both powdered and granular activated carbons were observed to be more effective than powdered and granular activated alumina. Mixtures of the adsorbents were no more effective than if the two had been used separately.

Fuchs (46) studied the effects of Ph and temperature on the adsorption of color from kraft caustic stage effluent, lime process effluent, chlorination stage effluent, and various combinations of chlorination, caustic, and hypochlorite stage effluents. He found that the adsorption of color from bleaching effluents is increased by decreasing pH and increasing temperature. The pH exerts the greatest effect on equilibrium, whereas the greatest effect of temperature is on the rate of adsorption.

McGlasson (72) also studied the treatment of various pulp and paper mill effluents with activated carbon. For comparative purposes, he treated kraft mill caustic bleach effluent with 15 g/l of lime as specified by Herbert (63) and with 10 g/l of pulverized activated carbon. Removal of color was comparable for lime treatment (95%) and activated carbon (90%). The lime treatment resulted in 45.5% removal of COD and 39% removal of BOD, whereas the carbon removed almost 80% of the COD and over 60% of the BOD. Table VII summarizes the results that were obtained (72).

Table VII

Lime and Carbon Treatment of Kraft Mill Bleach Plant Caustic Extract Effluent (72)

Treatment of sample	Color			C.O.D.			B.O.D.		
	Before trtmt.	After trtmt.	% Removed	Before trtmt.	After trtmt.	% Removed	Before trtmt.	After trtmt.	% Removed
15 g/l lime	9,750	500	95	1,603	875	45	260	159	39
10 g/l carbon	9,750	1,250	87	1,603	348	78	230	91	60

McGlasson also treated the caustic extract using lime and carbon treatment in series. The lime treatment was used ahead of the carbon treatment to remove the bulk of the color, and the carbon was used as a polishing agent. Using this treatment sequence, 99% of the color was removed as was 88% of the COD and 83% of the BOD. Studies reported by Smith and Berger (8) using a similar treatment sequence substantiated the reported capability of this scheme for removing BOD and color.

McGlasson also compared the capabilities of powdered and granular activated carbons in treating kraft mill total effluent. He found that a 10 g/l application of powdered carbon resulted in 98% color removal and 82% COD removal.

Lueck (68) has issued several reports on the use of granular activated carbon for treatment of sulfite condensate wastes. He reported that activated carbon adsorbed volatile organic acids and high percentages of the COD - causing materials quite efficiently.

Hansen and Burgess (12) evaluated the capability of granular activated carbon to treat kraft condensate wastes. Using two grades of granular carbon, they first pulverized and graded the carbons to a uniform size by washing through a 325 mesh sieve. The pulverized samples were then used for establishing batch-type isotherms on a condensate having an initial COD, BOD, and TOC of 910, 440, and 185 mg/l respectively. A dosage of about 2 g/l of carbon removed a little more than 60% of the COD and slightly less than 70% of the BOD and TOC. Extrapolation of Frendlich isotherms showed that the ultimate capacity of one carbon for COD should be 1.35 mg. COD/mg. carbon while the capacity of the second carbon should be 2.1 mg COD/mg. carbon. Column studies showed the capacities of the two carbons in the granular form were 0.7 and 0.96 mg. COD/mg. carbon.

Thibodeaux and Berger (9) have made pilot scale investigations of renovation of pulp and paper mill effluent in which activated carbon adsorption is one of the processes used in the treatment sequence. They performed trials on total mill effluents from an unbleached kraft linerboard mill and a bleached kraft mill, and on a bleached kraft mill caustic extract. The clarified effluents were subjected to lime treatment followed by biological oxidation and then adsorption by activated carbon in granular carbon columns. Tables VIII through XI summarize the conditions of each trial as well as the results (9).

The results shown in Tables VIII through XI indicate that the combined process of massive lime treatment, biological treatment, and activated carbon treatment is feasible on a pilot scale. The water produced by this scheme is practically free of all color,

Table VIII

Renovated Water Analysis (9)

Unbleached Kraft Linerboard Total Mill Effluent

Pilot Plant Run No. 1 50 Gallon Batch Operation

Constituent	Desired Range	Effluent	Obtained by Treatment		
			Lime[a]	Bio[b]	Carbon[c]
Turbidity, ppm	5-25	-	-	65	10
Color, units	0-80	4800	140	200	10
pH	6.5-7.7	8.7	11.5	9.1	8.7
Hardness, ppm $CaCO_3$	5-200	107	7.1	86	61
Dissolved solids, ppm	50-500	3380	2510	2650	2500
Chloride, ppm	10-150	110	140	36	36
COD, ppm	0-12	-	-	201	1
BOD, ppm	0-5	818	460	8	2
Na, ppm	-	1400	1130	1600(d)	1400

Notes: (a) 8.40 lbs, reburned lime slaked and added to raw effluent (equivalent to 20,000 ppm $Ca(OH)_2$).

(b) Extended aeration for 10 days. One gallon fertile lake water added as seed material. NH_4OH, HNO_3 and H_3PO_4 added as nutrient. H_2SO_4 added to Neutralize.

(c) Carbon columns containing 12x40 mesh activated carbon furnished by Pittsburgh Carbon. Contact time in the carbon bed was 8.2 minutes.

(d) Possible NH_4^+ interference.

Table IX

Renovated Water Analysis (9)

Unbleached Kraft Linerboard Total Mill Effluent
Pilot Plant Run No. 2 50 Gallon Batch Operation

Constituent	Desired Range	Effluent	Obtained by Treatment		
			Lime[a]	Bio[b]	Carbon[c]
Turbidity, ppm	5-25	-	-	-	-
Color, units	0-80	3000	100	200	15
pH	6.5-7.7	7.5	12.1	8.2	8.5
Hardness, ppm $CaCO_3$	5-200	-	964	1000	866
Dissolved Solids, ppm	50-500	4190	2610	3070	2800
Chloride, ppm	10-150	160	200	130	130
COD, ppm	0-12	-	-	-	-
B.O.D., ppm	0-5	1430	740	(135)[d]	(80)[d]
Na, ppm	-	320	230	230	230

Notes: (a) 2.87 lbs. reburned lime slaked and added to raw effluent (equivalent to 7500 ppm $Ca(OH)_2$).
(b) Extended aeration for 8 days. One gallon fertile lake water added as seed material. HNO_3, H_3PO_4 added as nutrient. H_2SO_4 added to neutralize.
(c) Carbon columns containing 12x40 mesh activated carbon furnished by Pittsburgh Carbon. Contact time in carbon bed was 1.6 minutes.
(d) Estimate, incubator problems.

Table X

Renovated Water Analysis (9)

Bleached Kraft Total Mill Effluent

Pilot Plant Run No. 3 50 Gallon Batch Operation

Constituent	Desired Range	Effluent	Obtained by Treatment			
			Lime[a]	Bio[b]	Carbon[c]	Ion Exchange[d]
Turbidity, ppm	0-5	85	35	35	35	0
Color, units	0-5	1000	90	60	15	5
pH	6.8-7.3	6.75	11.2	7.2	8.0	7.2
Hardness, ppm $CaCO_3$	5-100	-	85	75	64	-
Dissolved Solids, ppm	50-250	2000	1900	1790	1570	180
Chlorides, ppm	10-150	593	593	535	461	150
B.O.D., ppm	0-2	225	170	13	0	0
Sodium, ppm	-	310	310	310	310	65

Notes: (a) 5.9 lbs. reburned lime slaked and added to raw effluent (equivalent to 15,000 ppm CaO).

(b) Extended aeration for 6 3/4 days. One gallon fertile lake water added as seed material. HNO_3, H_3PO_4 added as nutrients. H_2SO_4 added to neutralize.

(c) Activated carbon of mesh 12x40 furnished by Pittsburgh Carbon. Contact time was 1.25 minutes.

(d) Quality data in this column are results of laboratory studies on the water obtained from the pilot plant after Activated Carbon Treatment.

Table XI

Renovated Water Analysis (9)

Bleached Kraft Caustic Extract

Pilot Plant Run No. 4 50 Gallon Batch Operation

Constituent	Desired Range	Effluent	Obtained by Treatment			
			Lime[a]	Bio[b]	Carbon[c]	Ion Exchange[d]
Turbidity, ppm	0-5	310	35	35	35	0
Color, units	0-5	12000	1100	1000	10	5
pH	6.8-7.3	12.6	11.25	9.2	8.7	3.7
Hardness, ppm $CaCO_3$	5-100	-	107	142	82	25
Dissolved Solids, ppm	50-250	5820	4320	3330	3930	250
Chlorides, ppm	10-150	1150	1320	1380	1250	120
B.O.D., ppm	0-2	420	210	40	7.6	0
Sodium, ppm	-	1200	1200	1200	1220	20

Notes: (a) 5.9 lbs. reburned lime slaked and added to raw effluent (equivalent to 15,000 ppm CaO).

(b) Extended aeration for 6 days. One gallon fertile lake water added as seed material. HNO_3, H_3PO_4 added as nutrients. H_2SO_4 added to neutralize.

(c) Activated carbon of mesh 12x40 furnished by Pittsburgh Carbon. Contact time was 7.12 minutes.

(d) Quality data in this column are results of laboratory studies on the water obtained from the Pilot Plant after Activated Carbon Treatment.

BOD, and turbidity. It is also evident that this treatment sequence does not materially affect the dissolved solids.

4. Application and Consumption Overview

The first major use of activated carbon in liquid purification was for the removal of color and other impurities in sugar refineries. Another major use of activated carbon, as discussed before, is the treatment of municipal water supplies for removal of tastes and odors (43). Sugar refining and municipal water treatment account for over half of the activated carbon used in liquid-phase processes. It is estimated that 50 million pounds of activated carbon (mostly powdered) was used in municipal water treatment plants in the United States during 1968 (105). The decolorization of sugar (both corn and cane) required an estimated 40 million pounds of activated carbon. In the past, sugar refineries mostly used powedered activated carbon, but the recent trend has been toward the use of granular activated carbon.

Use of activated carbon for gas adsorption and for solvent purification in the dry cleaning industry are about equal. The former is estimated to use 14 million pounds annually while the latter consumes about 13 million pounds (105).

Activated carbon is also used in reclaimed rubber in the manufacture of white sedewall tires. The addition of activated carbon to the black components of the tire prevents migration of the reclaiming oils into the white sidewalls and thus prevents staining. About 11 million pounds of activated carbon are estimated to be used for this purpose (105).

About 7 million pounds of activated carbon were used in the pharmaceutical industry in 1968. The carbon used by this industry is high purity, high cost, and is used to remove color and harmful biological materials from antibiotics, intravenous solutions, and synthetic vitamins.

The food industry uses activated carbons for a number of purposes (94). The major use is for removal of colored unsaturated polymeric pigments. Other uses reported for activated carbon in the food industry are:

(1) Removal of foaming compounds, color precursors and floc.
(2) Removal of impurities which would lower the yield and/or the purity of the product.
(3) Removal of impurities contributing to objectionable tastes and odors.
(4) Recovery of a product from a solution or solvent.
(5) Treatment of water or gases which eventually become a part of the product.

The use of activated carbon for removal of colors and flavors from scrap candies so that they can be reused is reported (105). Alcoholic

beverages are also purified with activated carbons.

Activated carbon is used in the manufacture of organics other than pharmaceuticals and food (43). It is used in the production of waxes and plasticizers where it aids in meeting color specifications.

The use of activated carbons in inorganic processes is reported. Liquid alum is kept clear by mixing activated carbon into the reacting batch of bauxite from which the alum is made (43). The electroplating industry uses activated carbon in a filtration-adsorption treatment to remove from plating solutions the organic impurities which would otherwise interfere with adhesion or brightness of the plate.

SECTION V

IN-PLANT WATER REUSE IN PULP AND PAPER MILLS

Present Water Reuse Practices

1. General Overview

Large quantities of water are used by the pulp and paper industry for cooling, washing, transporting, chemical preparation, and for other purposes. In fact, the paper industry is the third largest industrial water user (23). It has been estimated that approximately 2,100 billion gallons of water are used annually by the paper industry in the United States (75,14). It has further been estimated that water usage in terms of the sum of the water used at all individual water consumption points is close to 6,000 billion gallons annually. In other words, of the 6,000 billion gallons needed in the process, only 2,100 billion gallons are fresh water, while the other 65% of the water requirement is met by reuse. This means water goes through an average of three use cycles in the mill before being discharged. Another report indicated the percent of total process water reused ranged 63 to 72 percent, with kraft mills at the top of the range (40). Calculated as a percent reuse factor, that is, water reused divided by fresh water intake, bleached kraft pulp and paper had a 320% reuse whereas unbleached kraft pulp and paper had a reuse factor of 260%.

The fresh water intake by the pulp and paper industry in terms of gallons per ton of product has decreased significantly throughout the years. For example, from 1954 to 1964 the total tonnage of product increased over 52% whereas the total water intake increased by 16% resulting in a 23% reduction in water consumed per ton of product (14). It is expected that because of reuse, recirculation, and other water conservation practices the water intake per unit of product will continue to decrease.

As the preceding paragraphs point out, the pulp and paper industry actively practices water reuse. Clouse (23) reports that there are three apparent reasons for increasing water reuse: (1) economics; (2) public opinion, and (3) possibility of future shortage. The ultimate in water reuse would be to have no effluent at all, a fact that reportedly has been accomplished at one board mill in the Miami Valley.

Table XII depicts the sources of reuse water and the points of reuse as practiced in kraft or soda mills (87). The extent of reuse at any particular mill depends greatly on the product being made as well as on restrictions on water intake (59).

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Table XII

Reuse of Water in Kraft or Soda Mills (87)

Source	Reuse
Digesting, washing, and screening:	
Blow tank vapors condensate	Brownstock washing, shower water
Digester colling condensate	Smelt dissolving, dilution, deinking pulpers, woodyard
Turpentine separator underflow	Shower water in lime mud system
Decker or thickener water	Dilution water before screening and cleaning
Pulp mill condensates	Brownstock dilution
Condenser cooling water	Brownstock dilution
Paper machine white water	Brownstock dilution, washing and screening, recycled to machine
Evaporator condensates	Brownstock washing, dregs washing, mud washing, mud filtration, white liquor filter backwashing, deinking pulpers, hot pond debarking, grinders recovery furnace gas scrubbing
Causticizing and lime burning:	
Lime kiln scrubbing water	Recycled
Clarifier effluent from lime sludge	Recycled to kiln scrubber
Recovery furnace:	
Scrubber liquor following electrostatic precipitation	Recycled or returned to dregs or lime mud washing
Bleaching:	
Washer filtrate	Stock dilution
Excess washer seal box water	Seal box dilution
Cooling water	Bleaching tower dilution water
Chlorine dioxide spent liquor	Replace salt cake, tall oil soap acidulation
Power house cooling water	Process water
Other cooling water	Process water

Major sources of water for reuse in a paper mill have been identified as the paper machine white water, cooling waters, decker filtrates, combined condensates, bleach plant washer filtrate, and water from log flumes and barkers (23,40,80). Several authors have described and discussed limitations to the reuse of water (33,40,87,80,67,62,106). The following is a description of problems encountered when reusing water:

(1) Slime buildup, which slows drainage, causes lost production, plugs equipment, and makes dirty paper.
(2) Increased acidity resulting in corrosion, sizing, and color problems as well as decreased paper strength and poor aging properties of the paper.
(3) Buildup of dissolved solids causing foam and the problems attendant with foam.
(4) Deposition of pitch and/or beater size at the water line and on wires, rolls, and felts.
(5) Starch from broke which contributes to slime and foam, interferes with wire retention, and hinders saveall operation.
(6) Buildup of fines and colloidal particles which affects drainage and sheet characteristics.
(7) Temperature increase which may be either good or bad depending on the product.

2. Woodyard

The reuse of wastewater in the woodyard is an accepted practice (40). Specific usage areas are in log flumes, hot ponds, hydraulic or wet drum barkers, and for showers before chipping. Heated effluents such as evaporator condensates, bleach plant washer filtrate, and paper machine white waters are preferred because of the beneficial effect of increased temperature on bark removal efficiency (87). Recycling of woodyard effluent after grit removal is also practiced.

3. Pulp Mill, Recovery

From the pulp mill, combined condensates are increasingly being reused. In a 1957 survey (80), 23 of 30 southern kraft mills reported some reuse of this water. Combined condensate represents a high quality source of supply from the standpoints of heat content and low suspended and dissolved solids content. The major reuses of this water are in pulp washing and caustic room makeup (80,58). Other uses are in the woodyard, bleach plant, condenser water, and machine water. One report (40) indicated the condensate may be used in steam generation.

Decker filtrate is reused to a large extent (80). Reuse applications are many; it may be used for stock dilution, showers, pulp washing, groundwood grinders, screening, condenser water, fly ash control, woodyard, and general washup. The major areas of

reuse of this water are for stock dilution, screening, and as condenser water makeup.

In the kraft chemical recovery process, water is reused for dregs washing, green liquor dilution, lime slaking, lime mud washing, lime kiln scrubbing, white liquor filter back washing, and as flue gas scrubber water (40). The major source of water for these uses is the evaporator condensate, although other sources have been used for these purposes.

4. Bleach Plant

The quantity of water used in bleaching is quite high, the major volume being used to transport the fiber at low consistency. Gilmont (52) reported the results of a TAPPI survey of water requirements for bleaching. Table XIII depicts the water use in the bleach plant.

Assuming a maximum average consistency of 8% on the washer drums, theoretically each washing stage would require approximately 2,800 gallons of water to completely displace the water in one ton of pulp. Over half of the 52 mills which answered the TAPPI survey indicated that they used considerably less fresh water than that theoretically required for one complete displacement. The reuse of other water was reported to make up the additional volume.

Table XIII

Water Requirements in the Bleach Plant (52)

Function	Gal/ton pulp
Washer vat dilution (3%-1%)	16,000
High density stock dilution (12%-3%)	6,000
Washer showers: 1.0 displacement	2,800
2.0 displacement	5,600
Wire cleaning showers	100-600
Bleach chemical makeup	250-1,100
Heating, per hot stage	250

Market pulp mills use high quality white water from the paper machine extensively in the bleach plant, including use as dilution water for the transport of stock from the bleach plant to the paper machine. However, some paper mills reported reduced brightness and increased dirt count when paper machine white water is used in the bleach plant.

In several cases, tempered water from the heat exchangers is used for final stage washing in the bleach plant. Uncontaminated cooling water is sometimes used in the bleach plant with resultant heat savings (52,58). The heat economy gained can save boiler feed water lost through direct steam heating of stock.

Low quality water such as solutions from scrubbers used to trap escaping Cl_2 or ClO_2 are used on stages where corrosion is unlikely. Gilmont (52) also reported that filtrate from soda-base hypochlorite is reused very extensively for dilution on previous stages, brown stock dilution before chlorination, and for displacement washing.

A large number of mills reported little or no filtrate sewered from later stages of the bleaching operation. These filtrates are used countercurrently for dilution or, in some cases, for displacement washing. Filtrates may be matched by pH and temperature for use on previous stages, or they may be used countercurrently on preceding stage of different pH.

Gilmont reported that filtrate water is used countercurrently by various schemes. Overflow of filtrates to the seal box of the previous stage with all fresh water on displacement showers is one scheme. Another method is to use fresh water on the first displacement showers with filtrate on the following showers. Still another method is the use of filtrate on all showers with fresh water on wire cleaning showers only.

Although there is considerable interest in the use of chlorination stage filtrate, its actual use is limited, mostly to brown stock dilution. Most mills sewer the chlorination filtrate as well as the first caustic extraction filtrate.

5. Paper Mill

The greatest volume of fresh water in the pulp and paper mills is used directly on the paper machine and is introduced through felt and wire cleaning showers (84). Coats reports that water usage in cleaning press wet felts is the largest single consumer of fresh water on a new paper machine (24). Smaller amounts of fresh water are used for stock dilution and washing or cleaning the stock ahead of the machines. Auxiliary equipment also requires fresh water, and vacuum pump sealing water is the largest such use. Table XIV illustrates the water requirements of a 900 to 1000 ton/day linerboard machine, and indicates a fair degree of water reuse (24).

Table XIV

Clean Water Requirements for 340 in. Linerboard Machine (24)

Application	Demand, gal/min	Fresh Water, gal/min	Process Source, gal/min	Recirculation gal/min	Sewer gal/min
Gland seal water	595	595	-	-	445
Vacuum pumps seal	900	900	-	-	120
Press felt washing	1484	1484	-	-	-
Grooved roll shower	200	200	-	-	-
Miscellaneous	741	741	-	-	-
Cooling water	2360	-	-	2360	-
Miscellaneous paper machine showers	2215	-	2215	-	-
Cleaner dilution	200	-	200	-	200
Total, gal/min	8695	3920	2415	2360	765
Total, MGD	12.50	5.66	3.48	3.36	1.14

The reuse of white water is of economic importance as well as being an effective method for reducing pollution loads. Reuse of paper machine white water in stock preparation in integrated pulping operations is practiced to various degrees in pulp and paper mills (84).

To obtain maximum economic benefit, the most concentrated white waters are segregated and reused within their own stock preparation system. This practice results in maximum recovery of papermaking materials at the highest level of quality. Examples of concentrated white water that is reused are tray water, wirepit water, and couchpit water.

The normal procedure is to recirculate concentrated white water and use it as dilution water in beaters and consistency regulators and as makeup water for additives (90). When the water demand for these purposes has been satisfied, the remaining white water is sent to the saveall to reclaim the fiber and filler content.

The industry is currently using many types of savealls, filters, screens, clarifiers, flotation units and similar equipment to reclaim filler and fiber (14). Drum or disk vacuum savealls are more flexible than flotation savealls because of their ease of operation and capacity to take surges during paper breaks (24). The disk saveall is also proving more satisfactory because of the higher clarity of the effluent. One author reported reducing the suspended solids from 5-10 lbs/1000 gal to 2 lb/1000 gal on such a unit (106). Installation of such equipment can usually be justified on the basis of the value of recovered fibers. Use of the clarified water in showers is possible.

There are certain precautions in white water reuse that should be observed. Generally, suction box and suction roll discharges should be excluded from reuse unless measures are taken to prevent slime accumulation (84). White water storage tanks should be provided with adequate agitation to prevent or minimize the deposition of solids and formation of slime. Furthermore, the reuse of white water is not practical where water use is low or intermittent because of possible pipeline plugging.

As mentioned previously, vacuum pump seal water requirements account for a large part of the fresh water requirements on the paper machine. Reuse of vacuum pump seal water can be accomplished in two general ways (26). The pump water system may be considered in series with one or more other water systems or it may be considered a separate closed cycle.

If the vacuum pump seal water system is considered to be in series with another system, then reuse may be accomplished by the following methods:

(1) Feed the pumps with fresh water and discharge to another system.
(2) Feed the pumps with pre-used water and sewer the discharge.
(3) Feed the pumps with pre-used water and discharge to another system.

Vacuum pump seal water is used or may be considered for use on felt showers, grooved roll showers, process water, pulp mill (for example, turpentine condenser), woodyard, mill wash water, and in the white water system (26). Another method of reuse is to use the discharged high vacuum service seal water to seal low vacuum service pumps. Despite the 15-20^{o}F increase in temperature after the first pass through the high vacuum pumps, there is very little effect on the capacity of the low vacuum service pumps.

There are several reasons why the reuse of vacuum pump seal water on felt showers is especially advocated. The felt showers

frequently use more water than the pumps and can thus utilize the total discharge. The temperature of the water is beneficial and the two services are usually close together.

Another water reuse technique mentioned is the reuse of water from another source for vacuum seal water. Some pre-used sources are power house condenser cooling water, bearing cooling water, clarified or fully treated effluent, drainage from log pile spray, and white water.

Sometimes vacuum pump seal water requirements are reduced by recirculating the water over a cooling tower or through a heat exchanger. Some fresh water is required in closed systems to purge contaminants.

6. Cooling Water

Cooling water is extensively reused and one survey showed that 27 of 30 reporting southern kraft mills employed some recycle of this stream (80). Cooling water is being reused in the fresh water system, for stock dilution, pulp washing, wood washing, flume water, fly ash control, and for recycle.

Potential Reuse and Water Conservation Methods

Fresh water consumption can be considerably reduced by proper design and maintenance. Thus the installation of inexpensive flow control and regulating devices in individual supply lines to packing glands will greatly aid in water conservation (24,90). Ross (90) advocates a loop system for mill water headers because of less fluctuation in header pressure even under extreme conditions of flow variations. This is beneficial because operators will tend to adjust manually controlled valves for the desired flow at minimum pressure. At maximum pressure, the flow will be greater and the excess represents waste.

Another aid to conserving water is the use of low-volume, high-pressure showers. Ross (90) reports the use of saturated steam on a wire shower to decrease water consumption. Shut-off valves at the free ends of wash hoses aid in water conservation, and the use of thermostats on water-cooled equipment such as air compressors would help to conserve water in many cases. The use of an automatic control on vacuum pumps to make seal water flow independent of water supply pressure is also advised (26). On low vacuum services (12 in. Hg and lower) it is possible and practical to reduce the flow below manufacturers specifications. A 30% reduction of water flow on low vacuum service pumps would decrease the vacuum by two-tenths of one inch Hg.

Several reuse and recycle possibilities, some of which are used to a limited extent now, have been suggested for further consideration (100):

(1) Cooling water, including vacuum pump seal water, pump bearing water, and air conditioning cooling water to be recycled to cooling pond or tower.
(2) Use of activated carbon adsorption to control dissolved organics buildup in closed recycle systems. Use side-stream treatment to minimize equipment size.
(3) Removal of organics from turpentine underflow, possibly by steam stripping or activated carbon treatment (see also ref. 12,33).
(4) Reuse of blowdown stream from white water on pulp washer.
(5) Use of evaporator condensate, after organics removal, in pulp washing and as make-up water for paper machine showers.
(6) Possibly close the woodyard water cycle, which requires solids separation.

Rapson (39) has suggested the recovery of bleach plant effluents. His suggested system has three essential components:

(1) Replacement of chlorine by chlorine dioxide in the chlorination stage to the maximum economically feasible extent to minimize chloride ion buildup.
(2) Countercurrent washing of the unbleached and bleached pulp with the minimum amount of water which will give high quality bleached pulp.
(3) Separation of sodium chloride from sodium sulfate in the furnace flue gas.

Rapson proposes to wash the bleached pulp with evaporator condensate that has been oxidized with chlorine and chlorine dioxide. Furthermore, the combined bleach plant effluent would be used to wash unbleached pulp. Some of the bleach plant effluent could be used to wash the lime mud and dregs and then to dissolve the smelt to make green liquor.

SECTION VI

EFFLUENT COLLECTION SYSTEMS

Effluent collection systems in pulp and paper mills are variable, but an increasingly common practice is to discharge wastes into separate sewers according to the strength and characteristics of the wastewater (40). For example, St. Regis' Ferguson mill at Monticello, Mississippi, has five separate sewers (36):

(1) Surface runoff and cooling waters sewers.
(2) Inert wastes sewer - green liquor dregs and bark boiler ash are pumped through separate lines to an ash pond.
(3) Low solids sewer
(4) High solids sewer
(5) Sanitary effluent

A Texas bleached kraft mill reports that their wastes leave the mill in four streams (89). There is a high BOD stream which receives clarification and biological oxidation. The settleable solids stream requires clarification and some biological oxidation, while the bleach plant alkaline stream requires only biological oxidation. The fourth stream or acid stream requires no treatment other than pH adjustment.

Four general classifications of kraft mill sewer systems are: (1) low suspended solids, (2) high suspended solids, (3) strong wastes, and (4) sanitary sewers (50).

Low suspended solids wastes include bleaching effluents and evaporator condensates which do not require clarification. High suspended solids wastes are composed mainly of decker, paper machine, and woodyard effluents. Primary clarification is required after screening and grit removal. The strong wastes sewer catches floor drains, overflows and spills, and strong condensates. Some mills provide strong waste storage basins or tanks so that these wastes may be metered into the treatment system at controlled rates in order to prevent an upset in treatment operations. Sanitary sewage is often not segregated since it can be effectively treated in the biological oxidation process. Where local receiving water standards require disinfection of wastes containing sanitary sewage, separate treatment facilities are provided, normally the packaged activated sludge treatment type. These provide chlorination for bacteriological control.

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SECTION VII

SOLIDS REMOVAL (PRIMARY CLARIFICATION)

Removal Requirements and Extent of Practice

Pulp and paper mill effluents contain suspended solids such as fiber, fiber debris, bark particles, shives, grit, and fillers or coating materials such as clay and calcium carbonate. Although most of the filler and fiber is removed, for economic reasons, in some type of saveall device before the carrying stream enters the effluent system, the effluent usually requires further clarification in order to reduce the pollution waste-load contributed by the suspended material. Suspended solids can form bottom deposits in receiving streams (54). These bottom deposits are harmful to aquatic life, unsightly, and form malodors upon decomposition, as well as exhibiting an appreciable demand for dissolved oxygen. Furthermore, highly dispersed materials such as fiber debris, filler, and coating material limit light penetration and thus retard the self-purification ability of a stream.

Solids removal (clarification, primary treatment) is widely practiced in the pulp and paper industry. Although sedimentation, filtration, and flotation are all utilized, the process most commonly used is sedimentation (38). A recent survey of the kraft industry by the National Council for Air and Stream Improvement showed that 82 of 113 kraft mills in the United States provide sedimentation facilities for effluent treatment (50).

Clarification is used primarily to treat those streams high in suspended solids. As indicated in the section on effluent collection systems, it is common to by-pass the solids removal treatment with effluents such as bleach plant filtrates which have a low settleable solids content.

Process Capabilities

Before discussing the capabilities of solids removal facilities, a clear delineation must be made between total suspended solids and settleable solids. The total suspended solids are all the solids in suspension in an effluent. The settleable fraction is defined as that which separates from the liquid in one hour of quiescent settling in a laboratory vessel, usually an Imhoff cone. In terms of total suspended solids, the efficiency of any clarification system will depend on the fraction of settleable solids present.

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Generally, sedimention of paper mill effluents without coagulant addition removes 70 to 80% of the total suspended solids while 90% or more reduction may be achieved with the aid of coagulants (49). Although the reduction in total suspended solids is variable, Edde (38) and Gehm (49) both report that properly designed clarifiers can be expected to remove more than 95% of the settleable solids.

Primary treatment also results in some reduction of five day B.O.D. As pointed out by Edde (38), the B.O.D. reduction depends on the type of mill and type of solids being removed in the primary treatment. For instance, a white water low in dissolved organic matter and containing fiber which readily settles will exhibit high B.O.D. reduction when clarified. Conversely, there would be little reduction in B.O.D. of a waste containing a large amount of dissolved organic matter and containing appreciable quantities of dispersed organics. In Edde's survey which included several types of mills, the B.O.D. reduction ranged from 22% for pulp mill effluents to 84% for tissue mill effluent (38). Gehm reports that primary clarification results in approximately 15% B.O.D. reduction (50), while another source reports a reduction of 10 to 40% (40).

Information on C.O.D. reduction and color reduction was not available; however, estimates were published in one report (40). The C.O.D. was estimated to be reduced by 10 to 30% and it was estimated that the "true" or dissolved color was reduced 0 to 10%. True color is not removed unless flocculation has caused adsorption, so that the color adsorbed on floc particles will settle out of the wastewater.

Specific Processes and Present Applications.

1. Pretreatment

Due to the nature of pulp and paper mill wastes, it has been found advisable to perform certain operations, termed pretreatment, before the clarification process. The presence of large pieces of debris necessitates the use of bar screens which may be manually cleaned or automatically cleaned by devices such as traveling rakes. Bar screens with a spacing of 3/4 to 1-1/2 inches between bars are normally used for this purpose (40). Fine screening is not as commonly used as coarse screening for wastewater pretreatment in the pulp and paper industry. Many pulp mills and a large number of paper mills lose trash in the form of chips, bark, wet strength paper, and slivers that pass through an ordinary bar screen (38). Because this type of trash may cause pump and pipe plugging, it seems desirable to remove it, normally with a screen having openings of 3/8 to 3/4 inch. Several types of screens are available for fine screening:

(1) self-cleaning rotating discs
(2) vibrating screens
(3) traveling screens, and
(4) drum screens.

Where a considerable amount of silt is present in the effluent, grit removal is practiced as a pretreatment (50). Presently about 60% of the industry practices grit and debris removal (40). Grit removal chambers are installed after screening equipment to trap solids with a particle size of 6 to 150 mesh and a specific gravity greater than two (69). Grit chambers are designed for an effective velocity of 0.6 ft/sec and a detention time of about one minute (50,56). The grit chambers are cleaned periodically with a clam shell bucket or, in some cases, continuously by mechanical means.

Deaeration is another pretreatment process which is sometimes necessary to prevent fiber flotation in the clarifier (38). This is particularly true when white waters are treated alone, or when coagulants are used.

2. Sedimentation

Sedimentation is generally accepted for solids removal because under most circumstances it is less expensive than the other processes. It is also less sensitive to variations in flow and solids concentration and less attention and maintenance are required (38).

Sedimentation is accomplished in earthen-banked clarification basins and in mechanical clarifiers. Gehm (50) reported that 23 kraft mills in the United States utilize earthen basins while 59 mills employ mechanical clarifiers. The most widely used mechanical clarifiers are the circular, mechanically cleaned type, but reactor-type clarifiers, rectangular mechanically cleaned basins, and conical tanks without collector mechanisms are also used (49).

Earth embanked basins are generally designed for 12 hrs. detention when free of sludge (50). When cleaned at proper intervals, the earth embanked basins yield an effluent which is comparable to that produced by a mechanical clarifier - that is, it contains one to two pounds of suspended solids per 1,000 gallons (49). Earthen basins are difficult to clean and the cost is $10 to $15 per ton of dry solids removed (50). The use of earthen sedimentation basins is rapidly declining as mechanically cleaned clarifiers are becoming standard practice.

Although circular, thickener-type clarifiers are most widely used, excellent results have been achieved with rectangular

clarifiers (103). Edde (38) reports that in practically all situations, a design based on a hydraulic loading capable of removing 95 to 100% of the settleable solids (determined by one hour quiescent settling in the laboratory) results in adequate area to accomplish sludge thickening. It is generally agreed (50,38,30) that rise rates of 600 gal/sq.ft./day will produce a sufficiently clarified effluent in practically all waste waters. However, higher hydraulic loadings are reported and one source reports rise rates of 600 to 1000 gal/sq.ft./day with 800 being a common value (40).

Theoretical detention time in the clarifier is three to four hours (50) and, at 700 gal/sq.ft./day rise rate, side wall depths of 10 to 12 feet provide the necessary detention time as well as adequate volume for storage of sludge during the thickening process (38).

Increasing evidence has shown that a minimum clearance between the stilling well and the floor of the clarifier is necessary to avoid scouring the solids from the area of the collection sump (38). This should be about 12 feet in clarifiers 150 feet or more in diameter. Van Luven (103) believes that it is necessary to have a minimum side wall depth of 12 feet and a bottom slope of one to two inches per foot with a substantial sludge pit in the center of the clarifier. He states that the sludge pit should be five feet or more in depth and should occupy at least 25% of the diameter of the clarifier.

Gehm (50) reports that dual unit clarifier installations are gaining preference because, with one unit down for repairs, the other clarifier may be operated at a rise rate of 1200 gal/sq.ft./day and still provide reasonably good settleable solids removal.

Frequently when a single clarifier is used, an equalization basin is provided after the clarifier to protect the biological treatment process during periods of abnormal operating conditions or clarifier shutdown (50). Since the solids load to the equalization basin is only a fraction of the total solids load, it generally requires cleaning only once every several years.

The costs of solids removal by a clarifier are categorized by Edde into three groups as follows: (1) the cost of the clarifier including collector mechanism, wires, etc., (2) the cost of pumps and piping and (3) the cost of sludge handling equipment. Clarifier cost per MGD capacity decreases as the capacity increases. For instance, a unit for one MGD will cost about $24,000 while a twenty MGD unit will cost about $7,500 per MGD. Piping cost is generally about 10% of the total cost when the piping arrangements are simple, but for unusual conditions a generalization cannot be made.

Another recent survey (11) indicated capital expenditures in dollars per ton of capacity per day are $1,000 to $1,500 for mechanical clarifiers and $1,500 to $1,750 for mechanical clarifiers and dewatering. Operating charges ranged from 45 to 75 cents per ton for mechanical clarifiers and 55 cents to $1.30 per ton for mechanical clarification plus dewatering. Capital expenditure for clarification in earthen basins is $500 per pulp-ton of mill capacity per day, while operating charges are reported to be 25 to 30 cents per ton of pulp.

3. Filtration and Flotation

Filtration and flotation processes are also used to remove solids from pulp and paper mill wastes, although not as extensively as the sedimentation process. Filtration savealls utilize fine screens to recover the fiber and filler contained in white water. An example of the use of air flotation is the removal of very fine fibers and solids found in the effluent from some types of production (40).

4. Sludge Handling

Most of the sludges from the clarification of pulp and paper mill effluents can be thickened in the primary clarifier to the point where they can be mechanically dewatered (103). Edde's survey of the industry in 1964 showed that 30 out of 53 mills reporting practiced such thickening. Some of the problems that prevent sludge thickening in the clarifier are: (1) insufficient storage capacity, (2) lightweight rake mechanism, (3) pump unable to handle thick sludge, and (4) lack of a torque measuring device.

When sludge thickening is practiced, the clarifier scraper mechanism is of the heavy duty type designed with a torque rating of ten times the square of the clarifier diameter (50,38). Generally the units are equipped with a torque limiting mechanism to protect against overload.

The type pump used to remove sludge from the primary clarifier unit depends on the size of the clarifier and the characteristics of the sludge. Centrifugal pumps are generally used on larger units, while plunger pumps are used with smaller units (50). When the sludge tends to compact to high consistencies, screw or Moyno type pumps are utilized. Both the screw and plunger pumps require close attention when trash is in the sludge (38). Piping is arranged for ease of cleaning in case of plugging. A common problem in sludge drawoff pipes is undersizing which results in bridging at the entrance or excessively high head loss causing stoppage when heavy fiber loads are encountered (38). Oversizing of piping is preferred and pipe sizes for sludge drawoff lines are generally as follows: (1) 6 inches for 50 to 100 feet diameter units, (2) 8 in. for 100 to 200 feet diameter units, and (3) 10 inches for clarifiers greater than 200 feet in diameter.

Two recent papers contain excellent information on the handling, dewatering, and disposal of sludges resulting from solids separation (primary treatment) and biological oxidation (40,50). Due to pipe plugging and pump head loss, it is customary to remove sludge from the primary clarifier at 3 to 6% solids although the solids concentration at which the sludge can be withdrawn ranges up to 10%.

Sludge from primary clarification units normally does not require further thickening before dewatering. Several methods are used to dewater clarifier underflow and the selection of a particular method depends on the type, concentration and quantity of solids. These methods include sludge drying basins, vacuum filters, centrifuges and screw presses.

The underflow from secondary clarifiers is normally withdrawn at about 1% solids. Gravity thickening of secondary sludges having a volatile solids of 60 to 90% results in a 2.5 to 3% solids concentration at loadings of 10 to 20 pounds per square foot. If gravity thickening of secondary sludges is not feasible, it can be mixed and dewatered with primary sludge. Secondary sludges can also be thickened by dissolved air flotation or centrifugation. The former process yields a sludge of 4 to 5% solids, whereas the latter process is capable of obtaining 5 to 8% solids.

With certain exceptions, sludges resulting from high rate biological treatment may be dewatered in combination with sludges from the primary clarifier.

Where sufficient land of suitable topography is available, the cheapest method for dewatering primary clarifier underflow is in sludge drying basins. If sludges from biological oxidation are present, sludge drying basins cannot generally be used because of malodors resulting from decomposition of the sludge. Sludge drying basins are decanted periodically during periods of cold weather or high stream flow.

When basins become full, the nature of the sludge determines further treatment. If the underflow is free of fibers, it will lose more water through evaporation and drainage and will eventually become friable enough to be removed and used for landfill on wasteland. Underflows high in filler content drain slowly and form surface crusts which retard evaporation. Drying basins containing this type of sludge are frequently abandoned when they become filled.

Both primary and combined sludges are dewatered by vacuum filtration. Conditioning chemicals such as lime or polyelectrolytes are often required. The filter cakes obtained contain from 20 to 30% solids.

Horizontal solid bowl centrifuges are also effective dewatering devices for pulp and paper mill sludges. Primary sludges can be easily dewatered on a solid bowl centrifuge to between 20 and 35% solids. At a feed solids concentration of 5% and depending upon the fiber content, combined sludges can be dewatered to 15 to 25% solids. Biological sludges usually require the addition of polyelectrolytes, after which they can be centrifuged to 12 to 20%.

Compared to the vacuum filter, the centrifuge requires less operator attention, but is more expensive to operate because of higher power requirements. Power requirements are approximately 0.7 to 1.0 hp per g.p.m. of feed sludge.

About 30 to 35% of the industry utilizes mechanical dewatering in one form or another. When incineration is used as a means of final disposal, pressing of filter or centrifuge cakes is used as an additional dewatering step to increase the solids content to 40 to 50%.

Although dewatered sludge is in most cases disposed of by landfill, there is increasing interest in other disposal methods. Incineration of solid wastes resulting from sludge dewatering is increasing as land costs increase and availability of land decreases.

SECTION VIII

BIOLOGICAL TREATMENT

Treatment Requirements and Extent of Practice

Pulp and paper mill effluents contain dissolved and suspended organic substances, primarily in the form of solubilized wood components and of fibers that are intentionally or inadvertendly discharged from the processes involved in converting wood or wood chips into pulp and paper. Most of these substances have an effect on the ecology of the receiving river or water system. The effect may take several forms, e.g. depletion of oxygen due to biological oxidation of these substances; production of foul odors due to biological reduction in absence of oxygen; effects on the marine life due to toxicity of some substances or depletion of oxygen; excessive growth of algae; and others. The ecological effect is either in fact detrimental, or generally considered so, making it necessary to exercise control over it.

The most common measures of the actual or potential ecological effect of a mill discharge today are the biological oxygen demand (B.O.D.) both of the effluent itself and of the receiving stream after admixture of the effluent, and the dissolved oxygen (D.O.) content of the receiving stream at several points downstream from the effluent admixture point. Other measures are also in use, such as dissolved and suspended solids, conductivity, turbidity, and color.

Control measures exercised on the effluent today aim to achieve or maintain a reasonable ecological balance in the receiving stream as determined by state regulatory authorities. However, more and more, restoration and maintenance of the presumed natural state of the stream is becoming the aim of control measures. Because of seasonally varying river water flows and assimilation capacity, early control measures involved primarily regulation of the discharge volume into the receiving stream. This required the use of storage lagoons to accept a more or less constant mill effluent flow, while allowing a variable lagoon discharge flow.

The biological treatment of pulp and paper mill effluents is an outgrowth of the practice of lagooning wastes for controlled discharge to the receiving stream. It was found that during

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storage the B.O.D. was reduced, and subsequent investigations determined that this phenomenon is due to bacteria utilizing the organic substances as a food source. It was found that the oxidation rate in holding ponds is limited mostly by atmospheric reoxygenation and that fiber deposition in the basins is detrimental to the B.O.D. reduction. Decomposition of the fibrous material results in soluble constituents which raise the oxygen demand of the waste, hence the desirability of suspended solids and fiber removal as discussed in Section VII.

Several biological treatment processes are utilized by the pulp and paper industry. These methods are: (1) storage oxidation or stabilization basins, (2) aerated stabilization basins, (3) activated sludge, and (4) trickling filter. One report (40) indicated that in 1967 oxidation ponds were used by about 20% of the industry, whereas aerated lagoons and activated sludge were each utilized by about five percent of the industry. Trickling filters were used by less than five percent of the industry.

Gehm (50) reported that 55 out of 113 kraft mills in the United States are providing some form of biological treatment. The most widely used processes in the kraft industry are storage oxidation basins (26 mills treating 432 M.G.D.) and aerated stabilization basins (17 mills treating 470 M.G.D.). The activated sludge process is used by 9 kraft mills, whereas the trickling filter is presently being used by only 2 kraft mills.

Process Capabilities

The primary purpose of biological treatment is to remove soluble materials exhibiting a biological oxygen demand. Biologically inert or refractory compounds such as lignin derivatives are not effectively removed during biological treatment.

The degree of B.O.D. removal depends to a great extent on the process used as well as on the influent loading. It is reported (40) that 30 to 95% of the five-day B.O.D. can be removed in the various biological processes.

Biological treatment also removes some of the chemical oxygen demand (C.O.D.). The reduction of C.O.D. ranges from 20 to 70% for the various processes.

The true or dissolved color may be reduced to some extent during biological treatment. This is probably due to adsorption on the biological solids. It is reported that the activated sludge process may result in a 10 to 30% decrease in color whereas the other processes may result in a 0 to 10% removal of color. One mill reported an exceptional case where slightly more than 40% reduction in color occurred as a result of aerated stabilization basin treatment of unbleached kraft effluent (76).

Howard and Walden (64) reported on the pollution and toxicity characteristics of pulp and paper mill effluents. Laboratory-scale activated sludge fermentation of bleach plant wastes was performed. The untreated wastes exhibited 96-hour median tolerance limit ($T.L.m._{96}$) values of 84.8, 77.1 and 77.1% for three samples. (The median tolerance limit is the concentration in percent by volume which will kill 50% of the exposed marine population in a known exposure time). There was no mortality among fish held in 100% treated effluent. Their study indicated that biological oxidation would reduce the inherent toxicity of pulp and paper mill bleach plant wastes.

Pulp and paper mill wastes are generally deficient in nitrogen and phosphorus, and these nutrients have to be added to obtain effective biological oxidation of waste. The normal amounts of nutrients per 100 lb. of B.O.D. are 5 lb. of nitrogen and 1 lb. of phosphorus (50). These nutrients are generally added in the form of ammonia and phosphoric acid. The ammonia may be added as either a liquid or a gas, depending upon availability and quantity requirements (40). It is reported that the presence of large amounts of alum in the waste water causes a larger demand for phosphoric acid because of the formation of insoluble aluminum phosphate.

Biological oxidation is generally performed on the total mill effluent after those streams that are high in settleable suspended solids have been treated for the removal of these solids. The desirability of keeping fibrous sedimentation from occuring in biological treatment facilities is recognized and as explained in a previous section, an equalization basin is generally provided ahead of biological oxidation. This basin provides additional settling and holding capacity to prevent an upset in biological treatment in the event the clarification system becomes overloaded or is down.

Specific Processes and Present Applications

1. Storage Oxidation or Stabilization Basins

Storage oxidation basins serve a dual purpose. They are used to regulate discharge to the receiving stream as well as to reduce the B.O.D. load. Gehm (50) reports that in some instances the basins are also used for cooling some of the spent process water being returned to operate evaporator jet condensers. One mill reportedly uses the stabilization basin to store process water intermittently on a seasonal basis.

The design of stabilization basins varies considerably. Some basins have been built which conform to the topography of the land; others have been built using dikes. Those basins which have utilized the land topography are quite variable in depth as well as in storage period and surface loading (50). Basins which have been built by dikework have been designed with depths of three to five feet and large surface areas, thus aiding reoxygenation.

Stabilization basin design basis is usually to pounds of B.O.D. per acre per day for B.O.D. removal of at least 85% (37). Basins have been designed for 10 to 300 pounds of B.O.D. per acre per day, with loadings of less than 50 pounds of B.O.D. providing removal of 90% or more of the five-day B.O.D. during the summer months. At high B.O.D. loadings the removal efficiency levels off at approximately 60 to 70%. Removal of up to 150 pounds of B.O.D. per acre per day have been accomplished by using very shallow multiple basins in series; however, anaerobic odor production is noted where loadings result in removal of more than 60 pounds per acre per day. The retention time in stabilization basins is usually 10 to 30 days. Table XV lists performance data on several basins (49).

Table XV

Effectiveness of Stabilization Treatment (49)

Type Mill	Type Treatment System	Pond Area, Acres	Maximum Retention, Days	B.O.D. Influent mg/l	B.O.D. Effluent mg/l	B.O.D. Removal %
Newsprint	Multiple plus Flowage	100	20	200	40	80
Newsprint	Single	140	15	180	110	39
Bleached Kraft	Single	215	30	299	157	48
Bleached Kraft	Single	175	35	108	36	67
Unbleached Kraft	Multiple plus Flowage	350	82	200	20	90

Edde (37) reports several reasons for the selection of stabilization basins as a biological treatment system. Among the reasons are: (1) responsiveness of effluent to treatment, (2) reliability of the process, (3) flexibility, and (4) low capital and operation cost. Gehm (49, 50) also points out that no mechanized quipment or operator attention is required.

The greatest disadvantage of stabilization basins is the requirement for large land areas of correct topography and imperviousness. Typically, 40 to 50 acres of pond area is provided per MGD of mill waste water (40). Consequently, stabilization basins are generally

limited to southern mills in the United States where large tracts of suitable land are available. Also, in the South, high ambient temperatures are conducive to microbiological action during most of the year.

The cost of stabilization basins is dependent upon local land values (37). Blosser (11) reports a cost of 25 to 35 cents per ton of pulp production capacity for non-aerated stabilization basins.

2. Aerated Stabilization Basins

The aerated stabilization basin evolved from the need to upgrade the biological treatment performance of overloaded stabilization basins. Aerated stabilization basins have been rapidly accepted and extensive use of this type of biological treatment is found in the pulp and paper industry. Seventeen kraft mills are using aerated stabilization basins to treat 450 to 470 MGD of waste water (50, 37).

The aerated stabilization basin requires much less land than storage stabilization basins. Typically, land usage may be two acres per MGD as compared to the 40 acres per MGD generally used in stabilization basins.

A design parameter that is often used in the construction of aerated stabilization basins is the Alpha value. The Alpha value is the relative ease of oxygen transfer in a waste as compared to pure water. Edde (37) reports that NCASI studies have shown that Alpha values range from 0.7 to 1.0 for kraft wastes, and generally as oxidation proceeds, the Alpha value approaches 1.0. If no experimental data are available, an Alpha value of 0.7 will provide a sufficient margin of safety when designing the aeration system.

Oxygenation is accomplished by mechanical or diffused aeration units and by induced surface aeration. Although the turbulence level in aerated basins is quite enough to distribute oxygen throughout the basin, it is insufficient to maintain all the bacterial solids in suspension. The aerator also helps to distribute the influent B.O.D. load throughout the basin (37).

Aerators may be pier-mounted or float-mounted with float-mounting favored for large basins because of wind effects and for flexibility (50). Gehm reports that for initial design purposes an aeration capacity of one to two pounds of oxygen per horsepower hour is generally employed. This figure takes into consideration the Alpha value, mixing, oxygen saturation, and effluent temperature.

Aerated basins are usually designed as a completely mixed system, thus a single basin without baffle walls is all that is required. Gillman (51) reports that dissolved oxygen levels of 0.5 ppm are adequate to maintain aerobic conditions.

Optimal ratios of B.O.D. to nitrogen-containing nutrients (as N) have been found to range from 50:1 with four days aeration to 100:1 with 10 to 15 days aeration (37). If aeration is extended beyond 10 to 15 days nutrient addition is not normally required.

The biological sludge produced in aerated stabilization basins is less than in the high rate biological processes. Normally 0.1 to 0.2 pounds of sludge are generated for each pound of B.O.D. removed (50, 107). Some of the sludge that is formed is consumed by endogenous respiration, some carries over in the effluent, and some settles in the basin. That portion which is not destroyed by endogenous respiration adds 0.1 pound of five day B.O.D. per pound of volatile suspended solids.

Operating costs of aerated stabilization basins are about $1.50 to $2.00 per ton of production, or 2.5¢ to 4.5¢ per pound of B.O.D. removed (37). Installed aerator costs have been reported as $250 to $350 per rated horsepower by Gehm (50) and $200 to $400 by Edde (37).

3. Activated Sludge Treatment

Experimentation on the feasibility of the activated sludge process for the treatment of kraft pulping wastes was started in 1948 (49). In 1953 the activated sludge process was first used to treat pulp and paper mill wastes.

Edde (37) reported that 14 mills are using the activated sludge process and Gehm (50) reported that nine kraft mills are using the process. A total of over 200 MGD of waste is treated in this manner and individual plant sizes range from 30,000 to 63 million gallons daily capacity.

The activated sludge process centers around the mass of settleable solids which forms when a biodegradable waste containing microbes is aerated. Known as activated sludge, the mass of settleable solids which forms consists of bacteria, protozoa, rotifers, fungi, and on occasion, nematodes. Gurnham (23) reports that at least 50 different types of bacteria have been found in various sludges, although not all types are present in any one sludge.

Several physical and chemical mechanisms have been ascribed to the removal of B.O.D. in an activated sludge treatment system (54). These are: (1) trapping of organic suspended matter in the biological floc, (2) physicochemical adsorption of dispersed material on the bacterial floc, (3) enzymatic adsorption of soluble organic matter by the microorganisms. The characteristics of the waste and the concentration of the active mixed liquor solids determine the time required for the reactions to occur.

The activated sludge process is a high rate process capable of a high degree of B.O.D. reduction. Three types of activated sludge processes have been used: (1) conventional system, (2) contact stabilization, and (3) completely mixed activated sludge.

Figure 4 is a simplified flow diagram of the conventional activated sludge process. Return sludge from the secondary clarifier is mixed with clarified waste before entering the aeration tank. Basically, plug flow of the mixed liquor with some longitudinal mixing occurs in the aeration tank (37). As mixed liquor flows through the aeration tank, the removal of organics occurs progressively, and the oxygen utilization rate decreases and approaches the endogenous level at the exit.

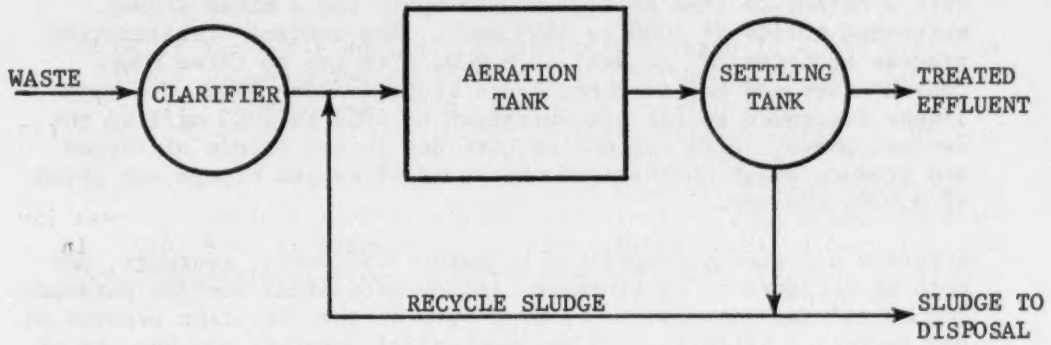

Figure 4

Conventional Activated Sludge System

The contact-stabilization process consists of mixing the waste with activated sludge for 15 minutes to one hour during which time organics are adsorbed. The sludge is then separated from the effluent in a clarifier and reaerated in a separate tank to stabilize the adsorbed organic matter. If the sludge is insufficiently aerated, its adsorption capacity is decreased because of the remaining unoxidized organics, and the B.O.D. removal efficiency of the system decreases. Overaeration is also harmful because overaerated sludges disperse and lose their high initial removal capacity.

The contact-stabilization process was originally developed to treat waste containing much of the B.O.D. as suspended or colloidal material. Because the stabilization of these materials occurs at much higher organism concentrations, the contact-stabilization process requires less tank volume than the conventional process. Another advantage is that the mass of biological organisms is outside the main waste water stream (40). Thus, if toxic or upset conditions occur, the system can be returned to its original conditions in less time than required by the conventional system.

The completely mixed activated sludge process mixes the raw waste uniformly with the entire contents of the aeration tank. The result is that the aeration tank acts as an equalization basin to smooth out load variations and dilute slugs and toxic materials (37). Higher organic loadings can thus be handled in this process than in the conventional activated sludge system.

It is reported that the conventional activated sludge process is particularly suited to treat waste water from sulfite mills, whereas the contact-stabilization process is particularly applicable to integrated kraft mill effluents (40). Removal of 85% of the B.O.D. may be attained by the conventional activated sludge process with a detention time of four to six hours and a mixed liquor suspended solids of 2000 to 3500 mg/l. The contact-stabilization process achieves 85% removal of B.O.D. with two to three hours contact time and two to three hours stabilization time at a mixed liquor suspended solids concentration of 2000 to 3000 mg/l in the contact phase. Both systems require one to two pounds of oxygen and produce about one-half to one pound of excess sludge per pound of B.O.D. removed.

Aeration has been accomplished by porous diffusers, spargers, and turbine aerators in combination, and by mechanical surface aerators. Mechanical aeration is now favored over diffuse aeration because of the increased efficiency of the mechanical aerators and because of the tendency of filter media to clog.

Addition of nutrients in the form of ammonia and phosphoric acid is generally required. Requirements are generally less than the theoretical optimum of 1 mg/l of nitrogen per 20 mg/l of B.O.D. and 1 mg/l of phosphorous per 60 mg/l of B.O.D., because of traces of these elements in most effluents (49).

Process loading of up to 150 pounds of B.O.D. per 1000 cubic feet aeration volume per day are reported. To achieve B.O.D. removals of 85% or better, loadings should not exceed 125 pounds per 1000 cubic feet per day. Furthermore, optimum sludge settling will occur in the final clarifier over a loading range of 0.2 to 0.7 pounds of B.O.D. per day per pound of mixed liquor suspended solids (37). Table XVI shows typical operating data from mill activated sludge treatment plants.

The activated sludge process is generally used where suitable land is not available for stabilization basins. Although the activated sludge process has been used successfully in treating most pulp and paper mill wastes, it has certain disadvantages. The capital cost involved is high, $55,000 to $150,000 per MGD hydraulic load or $50 to $62 per pound of B.O.D. per day (37). Operating costs range from $1.50 to $2.50 per ton of production or 3 to 5½ cents per pound of B.O.D. removed.

Table XVI

Activated Sludge Treatment Data (37)

Mill	Flow, MGD	B.O.D. #/ day	Detention Time, hr.	Loading #B.O.D./ 1000 cu. ft.	Loading #B.O.D./ #MLSS	MLSS mg/l	% B.O.D. Reduction	Nutrients
2	25	52,000	2.5	130	1.1	2,500	88	N,P
3	20	33,200	5.5	50	0.2	3,000	90	N,P
4	10.5	28,400	7.8	52	0.3	3,000	88	N,P
5	51	81,000	4.0	46	1.0	1,000	89	N,P
9	2.9	5,850	8.5	37.5	0.25	3,000	96	N,P

Sludge bulking is a common operating problem. Removal of the biological organisms is accomplished by gravity settling in a clarifier, generally designed for rise rates of 600 to 800 gallons per day per square foot. Gehm (50) reports that secondary clarifier rise rates should not exceed 400 gal. per day per square foot. Sludge bulking prevents effective settling in the final clarifier and as a result the final effluent has a high concentration of suspended solids. Edde (37) has suggested several causes for sludge bulking: (a) excessive filamentous bacteria, (b) overaeration, (c) underaeration and septicity, (d) too high or too low aeration solids content, or (e) nitrogen deficient waste. It is reported (40) that peripheral-feed, suction sludge draw-off clarifiers are being increasingly used as final clarifiers and that up to 98% of the solids are thus removed from the waste water.

4. Trickling Filters

Trickling filters promote contact between liquid waste and a biological growth. This is accomplished by allowing the waste to trickle down through a bed of crushed stone or plastic media to which the biological growth is attached. Aerobic conditions are maintained by the free passage of air through the trickling filter unit. Organic matter is consumed by the bacterial growth and converted into gases, dissolved substances and water, and solid residues of cellular material. The solids slough off into the effluent, thus clarification of the filter effluent is required. Periodic sloughing causes a wide variation in B.O.D. removal efficiency.

Although trickling filters are generally the most popular equipment for biological treatment of industrial wastes (56), they have only been used to a limited extent in the pulp and paper industry (37). Reasons for this lack of acceptance are concern over possible plugging of stone media

with fiber, high capital cost, and inability to accomplish high B.O.D. removal at high loading levels.

Trickling filters are capable of removing 40 to 50% of the B.O.D. at very high volumetric and B.O.D. loading levels. It is reported that trickling filters have proven useful where only partial B.O.D. reduction is needed or as a preliminary biological treatment prior to additional treatment, especially if cooling of the waste is beneficial. One such application is to use the trickling filter ahead of the activated sludge process (40).

Costs for plastic media trickling filter units are about $120 per cubic yard of filter media (37). Operating costs have been reported to be almost $2.00 per ton of production or 8 to 9¢ per pound of B.O.D. removed depending on amortization period, interest rate, labor and chemical cost. These costs do not include primary and secondary clarification.

SECTION IX

PRECIPITATION, COAGULATION, LIME TREATMENT

Overview: Extent of Practice

In this section, a general overview of the work and practice in this area is presented in Part A. The results that have been achieved on a laboratory or pilot basis, including lime treatment, are discussed in Part B. The present or planned large scale development and demonstration of several lime treatment processes receives additional separate coverage in Part C.

Coagulation techniques have been in use for years in water treatment plants to remove turbidity and colloidal color particles. The coagulants that are commonly used in water treatment are: (a) aluminum sulfate; (b) ferric sulfate; (c) ferrous sulfate; (d) ferric chloride; (4) ammonia alum; and (f) sodium aluminate (20,82). In addition to these materials, other materials known as coagulant aids are often used. The coagulant aids most often used are: (a) clays; (b) activated silica, and (c) polyelectrolytes.

Most of the coagulants used in water treatment as well as many other coagulating or precipitating agents have been investigated for the treatment of pulp and paper mill effluents. Foremost among the chemicals investigated were alum, ferric sulfate, lime, and various combinations of these (74). Fuller recently reported the investigation of a number of salts, mineral acids, waste pickling liquor, waste from alum manufacture, and waste from aluminum ore processing (47).

Coagulation and precipitation techniques are not widely used on a plant-scale for the treatment of pulp and paper wastes. It is estimated that approximately 5% of the industry utilizes coagulants (40). The most common use for coagulants is in the separation of solids from water for clarification or reuse purposes. One unbleached kraft mill is removing color from total effluent by the use of lime (83).

White water reclamation for reuse is accomplished by magnesium hydroxide precipitation by one mill having a limited fresh water supply (66). The process utilizes excess lime to precipitate magnesium hydroxide which flocculates suspended solids.

It is reported that polyelectrolytes are being used in the paper industry to improve white water clarification in savealls, to improve vacuum filtration of sludges, and to increase solids removal in mixed pulp and paper mill wastes (92). Other advantages of polyelectrolytes are claimed to be simpler handling and feeding equipment, and decreased tonnage of total sludge (solids plus coagulant).

Process Capabilities

Although coagulation is not extensively used on a plant scale in the pulp and paper industry, it has been widely investigated, and the capabilities of the process are fairly well documented. The following paragraphs describe some of the investigations and results which have been reported in the literature.

It is reported that investigation of the use of guar gums, synthetic polymers, and ferric sulfate showed that 20 to 40 mg/l of the coagulants was required to produce significant reductions in the color and suspended solids (25). The maximum B.O.D. reduction reported was 23%.

Rebhum, et al. reported that waste water from newsprint production is easily flocculated with alum and 30 to 40 mg/l is necessary to obtain a clear water (86). They also found that wastewater resulting from the manufacture of offset grade paper could not be flocculated with alum, sodium aluminate, lime, ferric sulfate, chlroine plus alum, chlorine plus ferric sulfate or various cationic, anionic, and nonionic polyelectrolytes. Further study using a synthetic colloidal system containing the components of offset white water showed that the high stability of the dispersion was due to an interaction between kaolin and pregelatinized starch. It was found that the addition of sodium bentonite clay caused a breakdown of the dispersion and brought about good flocculation and clarification.

The National Council for Air and Stream Improvement has evaluated 42 polyelectrolytes as coagulants in boardmill effluent (79). The most effective dosage was found to be 0.5 to 2.0 mg/l, and 1.0 mg/l gave consistently good results. Suspended solids removal increased from 88% without chemical addition to 94 to 96% with additions, producing a supernatant suspended solids concentration of 18 to 30 mg/l. The reported polyelectrolyte cost for treating this type waste water ranged from $5.50 to $14 per million gallons.

Middlebrooks, et al. reported investigation of alum and six organic polyelectrolytes, not previously used on pulp and paper mill wastes (25). The polyelectrolytes tested included anionic, nonionic, and cationic materials. The effectiveness of the various coagulants was judged by removal of suspended solids, C.O.D., B.O.D., and color. It was found that effective coagulation of the wastewater with the organic coagulants is dependent upon the pH of the effluent. Significant reductions in C.O.D. (54%), suspended solids (95%) and color (95%) of the kraft mill wastes were effected by alum and the polyelectrolytes; however, less than 20% reduction in B.O.D. was achieved.

Stemen (99) reported a unique method for the clarification of white water with the aid of a coagulating chemical. The process involves three steps, the first of which is the rapid mixing of white water with a coagulating chemical and a ferromagnetic powder. In the second step

the mixture is gently agitated to promote the formation of floc, and in the third step the floc is rapidly removed (5-25 seconds) by passing the waste over a magnetic drum. The process was tested in a 10 gpm continuous pilot plant using roofing mill waste. Removal of 30 to 50% of the B.O.D., 90% of the settleable solids, and 60 to 70% of the total suspended solids were achieved.

Several investigations of color removal by coagulation or chemical techniques have been reported. Moggio (74) reported the treatment of bleach plant wastes using lime, ferric sulfate-lime, and alum-lime combinations in the laboratory. Using lime alone, dosages ranged from approximately 860 to 3100 ppm, resulting in B.O.D. reduction of 2 to 15% and color reduction of 24 to 70%. Ferric sulfate-lime treatment, with the ferric sulfate application ranging from 172 to 860 ppm and the lime dosages from 687 to 1720 ppm, resulted in 2 to 18% B.O.D. reduction and color reduction of 34 to 84%. Alum-lime treatment using the same levels of dosage resulted in 0 to 18% reduction in B.O.D. and 45 to 80% color removal.

Moggio also treated mixed bleach plant-pulp mill wastes with the lime, ferric sulfate-lime, and alum-lime coagulants. Using various concentrations, up to 25% removal of B.O.D. and 91% removal of color were achieved.

The sludges which were obtained were gelatinous in nature and difficult to dewater. Lime had to be used with ferric sulfate to raise the pH and prevent the formation of highly colored iron-lignin and iron-tannin compounds. Lime was used with the alum to furnish the alkalinity necessary to precipitate the aluminum compounds.

Research by the National Council for Air and Stream Improvement and by several kraft mills further confirmed that color could be successfully removed from combined kraft and bleach effluents by lime precipitation. The sludge that was formed was found difficult to dewater to a dryness suitable for reburning in the kiln. Berger and Brown (7) reported on an attempt to alleviate the sludge problem resulting from color removal by lime. In laboratory and bench-scale pilot plant experiments, bleach plant caustic extract from a kraft mill was treated by application to a precoat of hydrated lime on a rotary vacuum filter. A reaction between lime and lignin occurs at the surface of the precoat, thus forming a film that can be doctored off to expose a fresh reactive surface. Although color removal in excess of 95% was obtained, cracking of the precoat during full pilot scale trials prevented further development of this method.

Clarke and Davis (22) investigated color removal from a kraft mill chlorination stage bleaching waste. Coagulants tested were $AlCl_3$, $Al_2(SO_4)_3$, and $Fe_2(SO_4)_3$. The pH of the $AlCl_3$ solution was adjusted by saturated $Ca(OH)_2$, whereas the pH of the $Al_2(SO_4)_3$ was adjusted with 0.1N NaOH. Polyelectrolytes or activated silica were added in some trials. The removal of total carbon (TC) and color in both systems

using Al^{+3} was found to be at an optimum in the pH range of 5 to 6, depending on salt dosage. In the $Al_2(SO_4)_3$ - NaOH system 87% of the color and 40% of the TC were removed by a dosage of 61 mg/l of aluminum ion. In the $AlCl_3$ - $Ca(OH)_2$ system 91% of the color and 42% of the TC were removed by a dosage of 40 mg/l of aluminum ion.

The removal of color and TC by $Fe_2(SO_4)_3$ is optimum in the pH range of 3.5 to 4.5 depending upon the salt dosage. At a pH of 4.5, a dosage of 112 mg/l iron is reported to remove 85% of the color and 48% of the TC.

It was found that neither silica nor organic polyelectrolytes had any significant effect on TC or color removal. However, both promoted flocculation and improved settling.

Smith and Christman (21) have also investigated color removal by coagulation. They investigated the use of alum and ferric chloride without the use of coagulant aids to treat sulfite waste, kraft waste (hardwood and softwood) and bleach plant caustic extract from hardwood kraft bleaching. It was found that both alum and iron coagulation of kraft wastes resulted in a dense rapidly settling coagulum. Optimum pH was found to 3.9 for ferric chloride and 5.3 for alum, whereas the optimum dosage was found to be a linear function of the initial color. Optimum pH and dosage resulted in about 92% color removal from the kraft wastes by alum and about 95% by ferric chloride.

Iron and alum coagulation of sulfite waste was not as effective as it was for kraft waste. Optimum dosages of alum resulted in only 67% color removal from sulfite pulping wastes. Trials with ferric chloride greatly intensified the color. When iron salts are used as coagulants, some of the color molecules react with iron to produce a highly colored complex. Although over half the initial color causing substance is removed (based on carbon measurement), the final effluent is more colored than the influent.

A recent investigation (47) has utilized various chemicals including mineral acids, various metal salts, waste pickling liquor, waste from alum manufacture, waste from aluminum ore processing, and alum. Alum was preferred by the investigator because of good color and B.O.D. reduction possible with it, and because it is present in the water treatment plant and in the paper machine effluents (101). The alum precipitation reduces the color of total mill effluent to a level where reuse, except perhaps in bleached grades, appears to be possible. Reduction in five day B.O.D. by alum precipitation was as follows: caustic bleach effluent, 80%; strong waste effluent 35 to 80% with an average of 50%; paper mill effluent 25%; size press and coating effluent, 50%; combined mill effluent, 25 to 80% with an average of 35 to 40%.

Some investigations have been made on the effect of specific white water components on the capability of coagulation. As mentioned before, Rebhun, et al. investigated the coagulation and clarification of white water containing pre-gelatinized starch (86). They found that pre-gelatinized starch caused a stable colloidal dispersion that could not

be broken by conventional inorganic or polymeric coagulants. Caron (18) reported the adverse effects on coagulation due to effluents from the coating operation. Coating room losses counteract the effectiveness of coagulants and cause increased chemical consumption as well as erratic results. Various authors have also reported that flocculants and retention aids were found to be inefficient in the presence of low concentrations of hypochlorite-oxidized starch (109). It is also reported that black liquor in waste has a dispersing effect on the solids, resulting in large dosage requirements of coagulants (92).

Lime Treatment Development and Demonstration

1. Review

Interest in the utilization of chemical treatment methods such as coagulation and precipitation for pulp and paper mill wastewater treatment has generally been aimed at removal of color, which is not amenable to biological degradation. Early laboratory investigations utilized coagulants and adsorbents that are known to be successful in color removal from natural waters (5).

As described in the preceding part of this section, various chemical treatment methods have been investigated and varying degrees of color removal were reported. Critical examination of the results showed that in all cases the quantity of chemicals needed to achieve the desired color removal resulted in excessive costs (73). In addition to the costs, certain technical problems became apparent. The greatest technical problem proved to be the large volume of gelatinous, difficult-to-dewater sludge that was formed. In addition to sludge disposal difficulties, some of the chemicals investigated would require corrosion resistant equipment.

Of more than 30 coagulants and adsorbents that were screened, it was determined that hydrated lime offered the best potential as a color reducing chemical for pulp and paper effluents (5). Lime was chosen for the following reasons: (1) ready availability and low cost; (2) highly-developed recovery techniques, using conventional recovery equipment available at kraft mills; and (3) the possession, by kraft operating personnel, of the necessary background and knowledge to successfully operate lime and recovery processes.

Further laboratory and pilot plant investigation of color removal from bleach plant caustic effluent by a minimum lime dose resulted in a gelatinous lime-organic sludge which could not be dewatered (73). An attempt to overcome the poor filterability of the lime-organic sludge led to development of the surface reaction technique. The surface reaction technique and the problem of precoat cracking were discussed in the previous section.

Further consideration of the sludge dewatering problem led to the development of the massive lime treatment process by the National Council (63). The massive lime treatment and the limited lime treatment processes

developed by Interstate Paper Company, Continental Can Company, and Georgia Pacific Corporation will be discussed separately, although all of these treatments utilize lime for color removal from pulp and paper waste water.

2. Massive Lime Treatment

The poor dewatering properties of lime-organic sludges resulting from limited lime dosages are caused by the organic matter that reacts with the lime to give insoluble calcium-organic compounds or that reacts and is adsorbed on the surface of the calcium hydroxide particles. The large lime requirements of the kraft chemical recovery operations provide a suitable source for obtaining lime concentrations sufficiently large so that the dewatering properties of the sludge can be enhanced by the presence of a large amount of $Ca(OH)_2$ particles which make the sludge denser and more easily filtered (63).

Since most of the lime so used for color removal would still be chemically available, it was suggested that the lime mud from the color removal step could be used in recausticizing green liquor. The available calcium hydroxide would be utilized for the conversion of the sodium carbonate to sodium hydroxide, while the lignin color bodies, which are soluble at the higher pH, would re-dissolve in the white liquor. It was expected that the dissolved organic matter would not be detrimental to the cooking properties of the white liquor, since it is common practice to dilute the concentrated white liquor with black liquor.

The considerations outlined in the previous paragraphs led to the development of the massive lime process, which is diagramed in Figure 5. Basically, the process consists of slaking and reacting the mill's total lime requirement with the highly colored caustic stage bleach effluent, settling and dewatering the resulting sludge, then using this sludge to causticize green liquor (63).

Laboratory and pilot plant tests showed the proposed process to be capable of removing 88 to 99% of the color, and 36 to 57% of the B.O.D. Clarification and filtration of the lime-organic sludge was reported as good (6).

Recausticizing efficiencies in mill tests ranged from 60 to 88% compared to normal mill practice of 67 to 87%. Organic-laden white liquor prepared by this process was used to cook pine and hardwood chips in pilot-scale digesters. The experimental pulps were tested and no significant differences in pulp quality were found.

Over 90% of the calcium in the decolorized filtered effluent was recovered in laboratory and mill pilot tests by adding CO_2 to convert the soluble $Ca(OH)_2$ to insolube $CaCO_3$. The results indicated that commercial clarifiers could be used for carbonation with the stack gas from mill lime kilns. The flocculation of the resulting $CaCO_3$ was found to be dependent on pH; below a pH of 11.5 the $CaCO_3$ is colloidal.

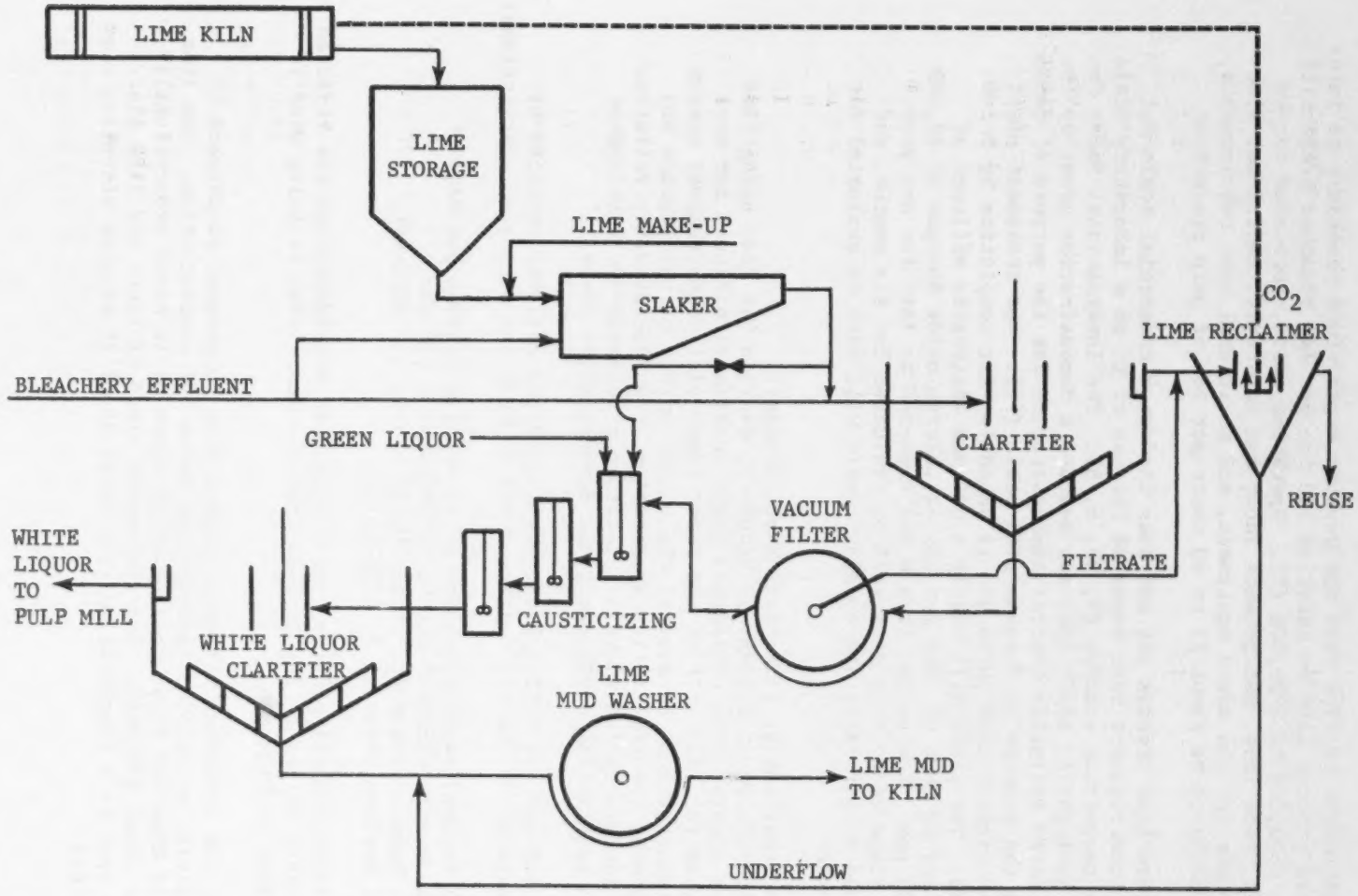

Figure 5
Massive Lime Process for Color Removal (63)

It was estimated in 1969 that the capital expenditure necessary to integrate this process into an existing 500 ton per day bleached kraft mill would be $600,000 to $700,000 (5). Operating costs, accounted for by lime loss, soda loss, maintenance labor and materials, additional electrical power for the added equipment, and additional heat requirements, was estimated to be about 25 to 40 cents per ton of pulp production.

The massive lime process has not been used on a commercial scale but several investigators have reported the use of it on a laboratory scale in water renovation studies (9, 95, 6, 8). The International Paper Company at Springhill, Louisiana, was awarded a demonstration grant by the Federal Water Pollution Control Administration for the purpose of demonstrating the process on a commercial scale (71). The treatment plant is in the construction phase and is scheduled for completion by December, 1969. The plant will handle a maximum wastewater effluent of 530 gpm and 63 tons of lime per day at calcium oxide dosages of 18,000 to 20,000 ppm. Evaluation trials are expected to last for one year. Caustic stage waste treatment will be evaluated for six months, and unbleached decker waste and combined waste will each be evaluated for three months.

3. Lime Treatment at Interstate Paper Company.
The Interstate Paper Company at Riceboro, Georgia has been using lime for color removal from unbleached kraft total mill effluent for more than a year (83, 32). It is the first commercial color removal system in the industry and, because of the unique nature of the process and industry-wide interest in its application, the Federal Water Pollution Control Administration awarded Interstate a research and development grant to help defray development and demonstration costs.

The 400 ton per day unbleached kraft linerboard mill was required by the Georgia Water Quality Control Board to meet the following restrictions:

(1) Maximum waste discharge of 10 million gallons per day.
(2) Maximum effluent B.O.D. of 800 pounds per day.
(3) Maximum suspended solids of 10 ppm in the effluent.
(4) Maximum color of 30 APHA units.

The National Council massive lime process was considered but was rejected on the basis of cost. The limited lime treatment that is being used is illustrated in Figure 6.

Lime for the treatment system is slaked with evaporator condensate to form a slurry of calcium hydroxide at about 15% concentration. The lime slurry is then fed to an in-line mixer where it is mixed proportionally with the total effluent. The thoroughly mixed effluent and lime slurry is then sent to a flocculation tank where about 75 minutes detention time is provided.

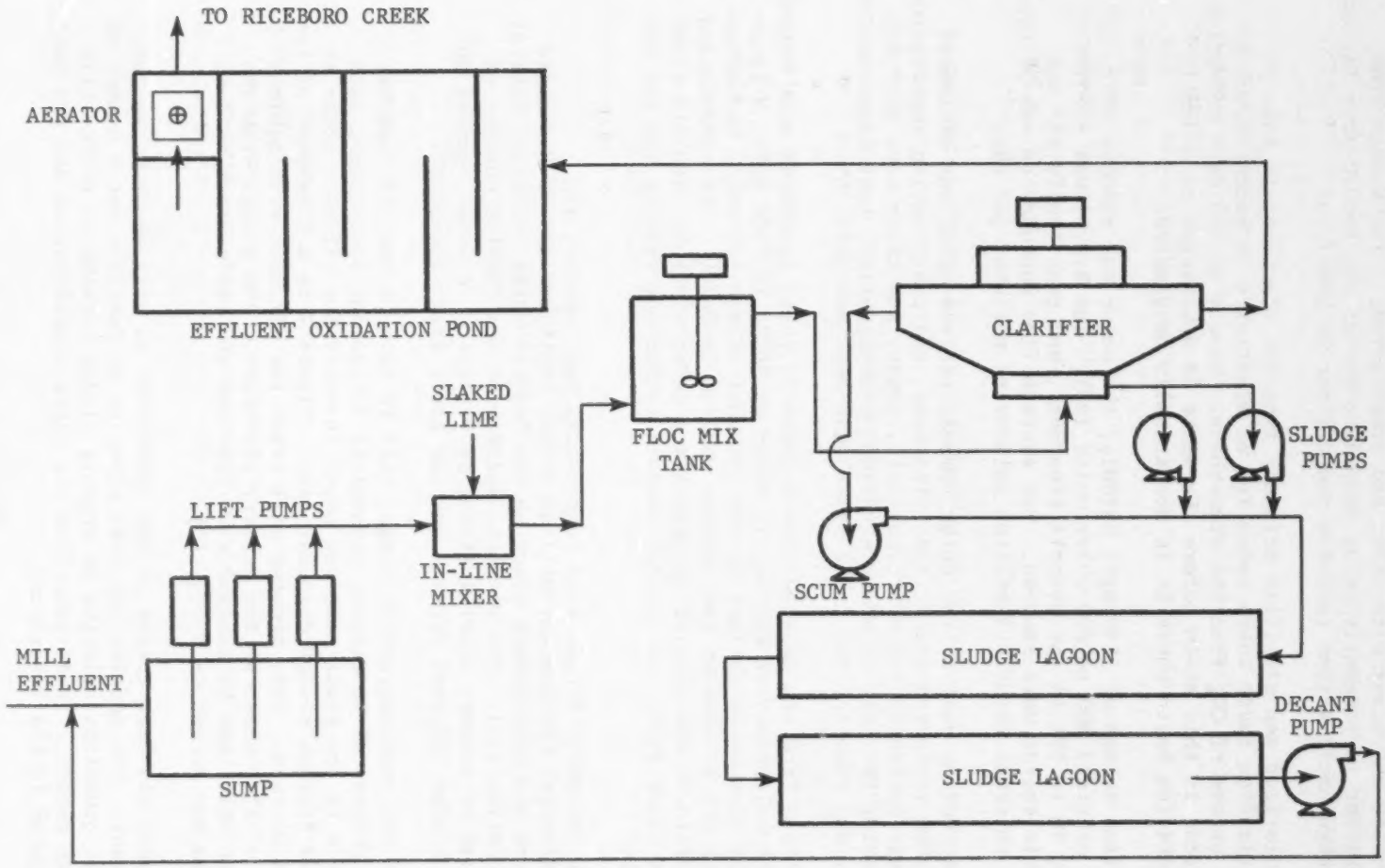

Figure 6

Line Treatment at Interstate Paper Corporation (83, 32)

From the flocculation tank, the waste flows by gravity to a 200-foot diameter clarifier. In the clarifier, floc from the color removal process settles out along with fiber and other solids. The sludge from the clarifier is presently being pumped to one of the two 20-acre lagoons for storage until a lime recovery process can be developed.

The decolorized and clarified effluent from the clarifier is sent to a stabilization basin where reduction of alkalinity is accomplished by natural uptake of CO_2 from the atmosphere. Ninety to 180 days retention is provided in this basin before the waste is discharged to a small final aeration basin where it is mechanically oxygenated.

With a lime dosage of 1650 mg/l $Ca(OH)_2$, the color was reduced 90 to 95% from an original 600 to 800 color units (83). The B.O.D. was reduced by at least 90 to 95% in the overall treatment, and practically all the settleable solids were removed. The average lime consumption was 37 tons per day to treat about 6.5 million gallons of effluent per day.

The construction cost of the color removal process plant was estimated at $454,100 including plans, specifications, and construction supervision. First year estimated costs of chemicals, power, and labor were $269,000. After adding the cost of administration, contingencies, post-construction studies, and reports, the total first year cost was $833,700.

The effluent from the massive lime process is fully saturated with $Ca(OH)_2$. Since the solubility of $Ca(OH)_2$ in water at 90°F. is 1500 mg/l, a large amount of lime would be lost in the effluent unless the water is carbonated with CO_2 to recover the soluble calcium as $CaCO_3$. The carbonation of the effluent was studied by Interstate under Grant No. WRD-813-01-68 from the Water Pollution Control Administration but results are not yet available.

4. Lime Treatment Proposed by Continental Can Company, Inc.
The Continental Can Company mill at Hodge, Louisiana has been awarded a research and development grant by the Federal Water Pollution Control Administration (41). The project, which will use limited dosages of lime ahead of primary clarification, is entitled, "A Color Removal and Fibrous Sludge Disposal Process for the Kraft Paper Industry".

Still in the preconstruction stage, this is to be a two year project for the purpose of developing economical design and operational data applicable to the kraft pulp and paper industry for effluent color removal and fibrous sludge disposal (41). Figure 7 is a flowsheet of the proposed process. This process will treat the effluent with minimum dosages of lime ahead of the primary clarifier. The sludge from the clarifier will then be admixed with lime mud and the mixture will be dewatered and burned in a kiln (5).

This scheme has been tested in the laboratory as well as in a two gpm pilot plant. The process has been shown to be feasible but a number of technical questions relative to organic sludge burning in a lime kiln have been raised. These questions are under consideration and are being investigated in the laboratory.

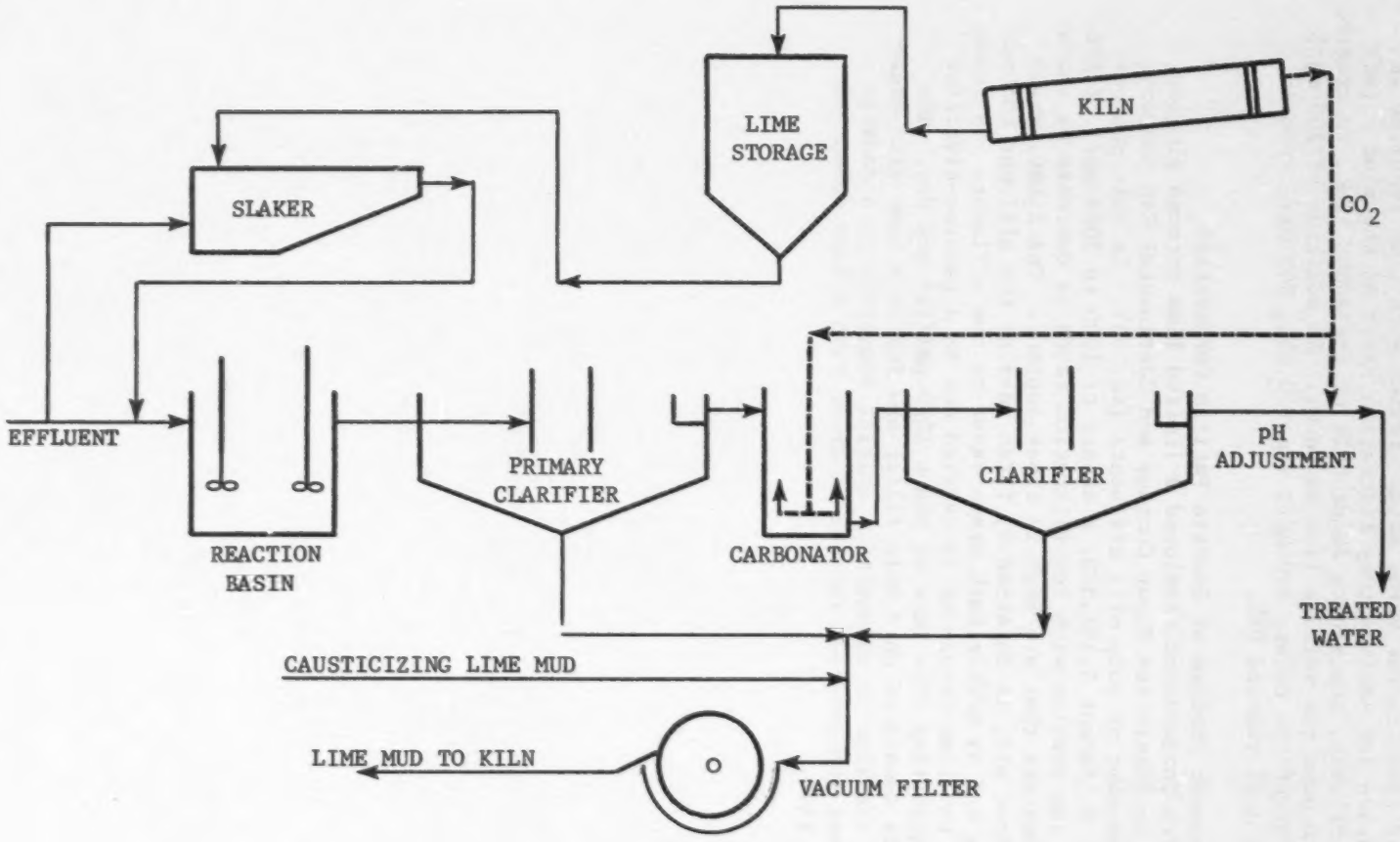

Figure 7

Continental Can Company, Inc. - Color Removal Process (5, 41)

Continental Can found that the inclusion of paper mill wastewater that contains fiber fines in the water being treated with lime resulted in good flocculation and satisfactory filtration rates of the sludge (98). The treated effluent, containing about half of the added lime, is treated with CO_2 to recover the soluble lime as $CaCO_3$. An addition of 200 mg/l CaO removed 30% of the color, 300 mg/l removed 65%, 500 mg/l removed 86%, and 1000 mg/l removed 91%.

5. Lime Treatment Process of Georgia Pacific Corporation

Georgia-Pacific Corporation developed a limited lime process similar to that used by Interstate Paper Company and Continental Can Company, Inc., for treatment of pulp mill effluents (48, 53). In this process, covered by U. S. Patent 3,351,370, a dosage of 1000 to 3000 mg/l of CaO is used, and the problem with low filtration rates is overcome by inclusion of wastewaters that are high in fiber content. The fiber, which acts as a filter aid, is obtained by first passing the effluent through log debarking and by adding bark press water to the effluent. As shown in Figure 8, the lime treatment is carried out in a reactor-clarifier which has a clarifier rise rate of about 1000 gal/ft^2 per day. The lime sludge is dewatered on a belt filter and fed to a lime kiln where about 80% of the lime is recovered. Initial operation on a caustic bleach effluent achieved 90% removal of color with a lime dosage of 2000 mg/l of lime.

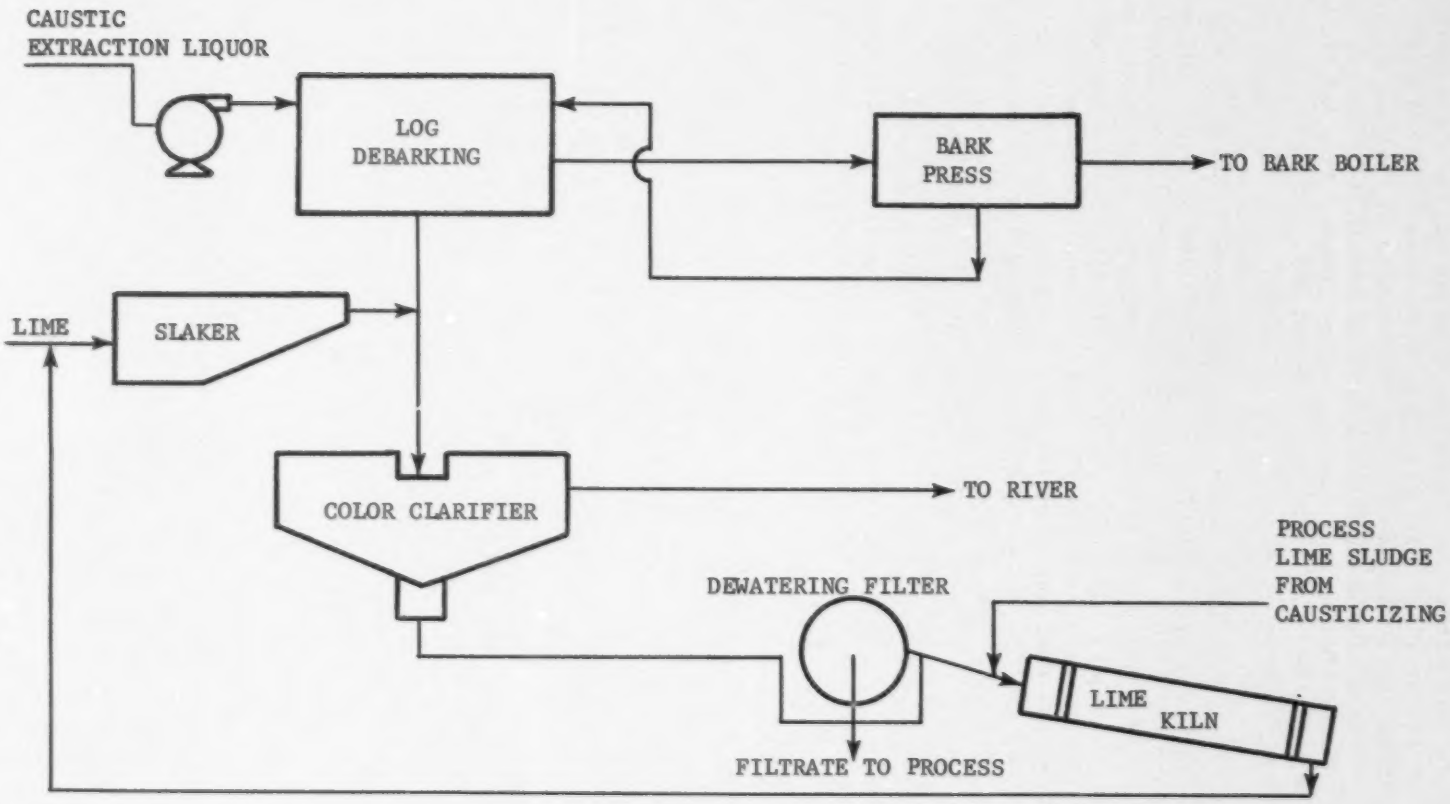

Figure 8

Georgia-Pacific Color Removal Process (48, 53)

SECTION X

OTHER TREATMENT METHODS

The purpose of this section is to briefly mention some waste treatment techniques that might possibly be used in the renovation of pulp and paper mill wastes for reuse, particularly those processes with potential application for dissolved inorganic salt removal. This section is not intended to present a comprehensive report on all the advanced waste treatment techniques that have been described in the literature, and as such, this section is a rather limited account of the selected treatment systems mentioned.

Hyperfiltration (Reverse Osmosis)

Hyperfiltration, or reverse osmosis, has undergone intensive development during the past ten years, primarily as a method for desalting water (85). It is the only membrane process which can be suitably adapted to the handling of industrial waste water (19). Several recent articles describe progress that has been made in utilizing reverse osmosis as a waste treatment process in the pulp and paper industry (108, 81, 3).

The Pulp Manufacturers' Research League has investigated the treatment of pulp and paper mill wastes by reverse osmosis under a project jointly sponsored by the League and the Federal Water Pollution Control Administration. Their extensive laboratory and pilot scale studies led to the design and construction of a portable semi-commercial test unit capable of processing 20,000 to 100,000 gallons daily.

Early laboratory scale investigations included treatment of pulping wash waters from acid sulfite, neutral sulfite and kraft pulping; sulfite bleach plant effluents from chlorine bleaching; and chlorine stage effluent and caustic wash waters from bleaching of kraft pulp; as well as barking effluents and sulfite process evaporator condensates (3). The study indicated the capabilities of reverse osmosis as a promising tool for the treatment of dilute pulp wastes. It was concluded (3) that:

(1) the nature of the waste stream in terms of its content of dissolved inorganic salts and of small and large molecular weight organics will materially affect operating conditions;
(2) as the concentration of the concentrate increase, the osmotic pressure also increases and the product flow rate decreases;
(3) the minimum linear velocity required for a dilute spent sulfite liquor increases with an increase in concentration of the concentrate;
(4) increased temperature of feed solution increases the product water flow rate; and
(5) rejection ratios for the organic components of the solution are high and stay high over the entire concentration range. The rejection of inorganic components is good, but the product water rates are more likely to drop at higher concentrations.

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Field tests of the portable commercial-scale unit (108) have been performed at three different sites. The first demonstration was conducted on dilute pulp washing effluent from a calcium base acid sulfite mill. The second demonstration was performed on the pulp wash water from on-machine washing of neutral sulfite semi-chemical pulp, and the third trial processed wash water from ammonia base acid sulfite pulping. Table XVII summarizes the results of the trials (108).

TABLE XVII

Summary of Results of Treatment by Reverse Osmosis (108)

Pulp Wash Water	Influent Concentrations, g/l				Average Rejections, %					Number of Samples
	Solids	BOD	COD	Base	Solids	BOD	COD	Base	OD*	
Calcium Sulfite	11.6	3.9	12.8	0.56CA	87	74	87	96Ca	96	17
Ammonium Sulfite	15.9	3.7	24.8	$0.36NH_3$	93	70	94	$90NH_3$	99	4
Neutral Sulfite	8.7	2.5	9.8	1.0Na	95	88	95	88Na	99	12

*Optical density at 281 nm (a measure of the lignosulfonate content).

As can be seen by the results summarized in Table XVII, the reverse osmosis technique certainly is worthy of further consideration. The field tests also pointed to certain shortcomings in terms of operating know-how and in the membranes. It was found in the first trial on calcium base sulfite wash water that when the concentration was much greater than 7% solids, there was a problem with $CaSO_4$ scaling. In the second demonstration (NSSC wash water), there was evidence of fouling, and the flux rates could not be sustained as high as had been expected. This forced a 33% reduction in feed rate, and it was not possible to sustain a 10% solids level even though there were no apparent scaling problems with this particular effluent. In the third demonstration, a persistent and increasing problem of membrane module failure occurred. Although there had been some membrane module failure in the first two trials, the problem became serious in the third demonstration. After nine months of operation 99 of the 387 modules had failed.

Perona, et al. have reported on the purification of sulfite mill wastes with a membrane dynamically formed from feed constituents (85). The dynamic formation of membranes is usually accomplished by circulating, under pressure, feeds containing additives of a colloidal nature past membranes having pores in the micron range. The additive concentrates at the interface and a purified solution permeates through the porous

membrane. Examples of additives that form dynamic membranes are Th(IV), Fe(III), and humic acid in aqueous solutions. Calcium-base sulfite liquors also form self-rejecting dynamic membranes, and the use of dynamic reverse osmosis membranes with such liquors has been studied and reported (85).

Dynamically formed membranes have the potential advantage of lower pressure requirements, higher production rates, and the rejection of neutral organic solutes as well as salts (85). Because of non-reproducibility of results, all the variables affecting the performance of these membranes are not yet under control, but preliminary laboratory studies have indicated that the process might be practical.

Cellulose acetate membranes have been used in most studies to date, and in general it can be said that these membranes reject the high valency ions better (13). The relative rejection of ions by cellulose acetate-based membranes has been studied and reported. It is reported (13) that the order of rejection of anions is as follows: citrate > tartrate = sulfate > acetate > chloride > bromide > nitrate > iodide > thiocyanate; where citrate is the most highly rejected ion. For cations the relative order of rejection is reported to be: magnesium = barium = strontium = calcium > lithium > sodium > potassium. It should be noted that the presence of other ions in solution can interfere with the relative rejections. For example, if the halides are present as salts the relative rejections are as listed above, but if they are present as halogen acids the order is reversed (13).

Reverse osmosis with cellulose acetate membranes does not effectively remove small water-soluble organic materials such as alcohols, aldehydes, low-molecular-weight organic acids, phenol, amines, and nitrites, as well as dissolved gases such as ammonia and carbon dioxide (19, 13).

Wiley, et al. (108) point out that the B.O.D. removal efficienty is dependent on the state of the B.O.D. forming components usually present in the waste. If wood sugars in the waste are allowed to be broken down by microbiological action during a prolonged processing time of more than an hour, the resultant low molecular weight degradation products, such as acetic acid, pass through the membranes and B.O.D. rejection is then quite low (108).

The cost of reverse osmosis has been estimated at about $1/1000 gallons of waste treated. In addition to the high treatment cost, it should be pointed out that the process not only yields a water suitable for reuse, but also produces an effluent stream having a concentration of dissolved substances about ten times greater than the original stream. Thus, further processing must be applied to the concentrated stream before any true pollution abatement can be realized.

Ion Exchange (Desal Process)

Although ion exchange has been widely used for many years in water treatment, it has been limited generally to waters containing less than 500 ppm dissolved solids because regeneration costs increase proportionately with the salinity (34). Thus, at higher dissolved solids, ion exchange can not economically compete with membrane and distillation processes. The DESAL process, developed by Rohm and Haas, is a new deionization technique based upon two weak electrolyte ion exchange resins. Some of the advantages over conventional ion exchange processes are claimed to be:

(1) Ability to deionize brackish waters (500 to 3000 ppm dissolved (solides) with negligible leakage.
(2) Stoichiometric amount of regenerants required for regeneration (conventional processes required 200 to 300% of the stoichiometric amount); thus regeneration costs are significantly lower.
(3) High degree of utilization of the theoretical capacity.

The DESAL process is a cyclic deionization process using three beds of weak electrolyte ion exchange resins. The first bed, which is the alkalization unit, contains a weak base anion exchange resin (Amberlite IRA-68) in the bicarbonate form. The second bed, or dealkalization unit, contains a weak acid cation exchange resin (Amberlite IRC-84); while the third unit, which is the carbonation unit, also contains Amberlite IRA-68, but in the free base form. Using the removal of NaCl as an illustrative example, the reactions which occur are as follows:

(1) Unit 1 (Alkalization): $(R\text{-}NH)HCO_3 + NaCl \rightarrow (R\text{-}NH)Cl + NaHCO_3$

(2) Unit 2 (Dealkalization): $RCOOH + NaHCO_3 \rightarrow RCOONa + CO_2 + H_2O$

(3) Unit 3 (Carbonation): $R\text{-}N + H_2O + CO_2 \rightarrow (R\text{-}NH)HCO_3$

When breakthrough occurs, the alkalization and dealkalization units are regenerated, for example with ammonia and sulfuric acid, respectively. Since the third unit is now in the bicarbonate form, the direction of flow is reversed and the cycle repeated.

It is reported that successful operation of the DESAL process has been achieved in two Italian pilot plants (34). A commercial installation in operation in the United States since September, 1966, has satisfactorily functioned in reducing a brackish water from 1000 mg/l to the 20 to 30 mg/l range.

Thibodeaux and Berger (9) have reported on laboratory investigations of this process to deionize partially renovated pulp and paper mill effluents. They worked with a bleached kraft mill total effluent and caustic stage extract which had been clarified and then treated successively by lime and activated carbon. The samples were virtually free of all color, B.O.D., and turbidity, but were unacceptable from the standpoint of

dissolved solids. Table XVIII shows the results of the trials (9). Of the parameters used to describe desirable process water requirements only the pH of the caustic effluent was out of the acceptable range. The low pH has been attributed to laboratory operating conditions and it is felt that under commercial conditions the system can produce a pH near 7.0.

It has thus been substantiated that this process is technically feasible for deionization of partially renovated waste water from pulp and paper mills. Operating costs of this process have been estimated at 24.0 to 27.5 ¢/1000 gal. (operating costs only), while installation costs, including equipment and resin, have been estimated at 0.8 MM dollars for a 2.0 MM gal/day plant.

TABLE XVIII

Water Quality From "DESAL" Ion Exchange Process (9)

Parameter	Desired Range, Bleach Mill Feed	DESAL Product	
		From Caustic Extract	From Total Mill Effluent (Bleached)
Color	0-5	5	5
pH	6.8-7.3	3.7	7.2
Cl, mg/l	10-150	120	150
Hardness, $CaCO_3$ mg/l	5-100	25	-
Dissolved Solids mg/l	50-250	250	180
B.O.D., mg/l	0-2	0	0
Turbidity, J.T.U.	0-5	0	0
C.O.D.	0-8	-	-

SECTION XI

ACKNOWLEDGMENTS

The authors gratefully acknowledge the invaluable contribution to this study made by the many people in operations, engineering, and research and development who made their time freely available early during the survey which has become part of this report. The list of these silent contributors is too long to mention specifically. It includes people from operating companies including St. Regis Paper Co., engineering firms, manufacturers of activated carbon, academic and federally sponsored research, development and demonstration facilities.

The National Council of the Paper Industry for Air and Stream Improvement (NCASI), particularly through H. F. Berger, Southern Regional Engineer, lent its assistance throughout the project.

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SECTION XII

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